Organic Syntheses via Transition Metal Complexes, CI[+]

Uncovering Reaction Pathways of 1-Aminocyclohexenes with [(1-Alkynyl)carbene]tungsten Complexes Leading to Cyclopentadienes and Dihydropyrroles

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Dedicated to Prof. W. P. Fehlhammer on the occasion of his 60th birthday

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Reactions of the [(1-alkynyl)carbene]tungsten complex $(CO)_5W{=}C(OEt)C{\equiv}CPh$ (**1**) with 1-aminocyclohexenes **2a–c** and **7a–c** afford different types of products depending on the amino substituents and the reaction conditions. (4-Aminocyclobutenyl)carbene complexes **B** have been shown to be generated in the first reaction step through a [2+2] cycloaddition. These are key intermediates and afford cross-conjugated tungstatrienes **E**, (conjugated) 1-tungsta-1,3,5-hexatrienes **G**, or (non-conjugated) 1-tungsta-1,3,6-heptatrienes **F** by following competing reaction pathways. Cross-conjugated 1-tungstatrienes **3** have been isolated in 52–74% yield by performing the reactions of 1-aminobenzocyclohexenes **2a–c** with compound **1** in pentane. In dichloromethane instead of pentane, (conjugated) 1-tungsta-1,3,5-hexatrienes **4** are obtained, which subsequently undergo fragmentation to give cyclopentadienes **6** (by π-cyclization) and dihydropyrroles (by α-cyclization) in a molar ratio dependent on the nature of the amino substituents. (Non-conjugated) 1-tungsta-1,3,6-heptatrienes **10** are generated upon reaction of 1-aminocyclohexenes **7a–c** with compounds **1**, which are transformed into cyclopentadienes **12** via conjugated 1-tungsta-1,3,5-hexatrienes **9** as intermediates. Reactions of 1-tungsta-1,3,6-heptatrienes **10** with the (1-alkynyl)carbene complex **1** afford dinuclear compounds **14**, which subsequently yield indenes **15** (by two successive π-cyclization steps) and *spiro*-tetrahydropyrroles **16** (by both a π-cyclization and an α-cyclization step), depending on the steric bulk of the amino substituent.

Introduction

(1-Alkynyl)carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CR$ (M = Cr, W) have been utilized as stoichiometric reagents in a number of high-yielding transformations of potential interest in organic synthesis.[2] We have been focusing on reactions of cyclic aminoalkenes with (1-alkynyl)carbene complexes, which were found to produce cyclopentadienes.[3] Whilst a smooth transformation of 1-(dimethylamino)cyclopentenes and 1-(dimethylamino)cyclohexenes into cyclopentadienes was achieved in dichloromethane solution under carefully controlled conditions, side reactions were observed (a) if the reaction was carried out in solvents other than dichloromethane, (b) if 1-aminocycloalkenes other than the dimethylamino derivatives were used, or (c) if the reagents were not applied in the stoichiometry and under the reaction conditions stated in ref.[3] We now wish to report on the nature of these "side reactions".

Addition of a 1-aminoalkene **A** (a = H, H; H, alkyl; ring chain) to the [(1-alkynyl)carbene]tungsten complex **1** affords a (4-aminocyclobutenyl)carbene complex **B** in the first reaction step. Compounds of this type have been isolated in two instances and could be characterized by crystal structure analyses.[4] They are stable in the solid state, but undergo rearrangement reactions in solution. The driving force for the rearrangement seems to stem from the 4-amino substituent, since related structures, e.g. the corresponding (4-alkyloxycyclobutenyl)carbene complexes, prove to be quite stable in solution. Two different routes (paths *a* and *b*) can be distinguished for the ring-opening of (4-aminocyclobutenyl)carbene complexes, both of which lead to zwitterionic carbiminium carbonylmetalates, i.e. **C** and **D**, respectively. The competing reaction pathways *a* and *b* are strongly influenced not only by substituents, but also by solvent effects. Several (conjugated) carbiminium carbonylmetalates **C** have been isolated and characterized by crystal structure analyses.[1,6b] Typically, they exhibit a strongly distorted ligand backbone, the geometry and pattern of bond lengths of which is significantly different from that in the case of cross-conjugated tungstatrienes **E**.[5] Though (non-conjugated) carbiminium carbonylmetalates **D** could not be observed, they are assumed to be common precursors to both (conjugated) 1-tungsta-1,3,5-hexatrienes **G** and (non-conjugated) 1-tungsta-1,3,6-heptatrienes **F** (Scheme 1).

[+] Part C: Ref.[1]

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[++] Crystal structure analysis.

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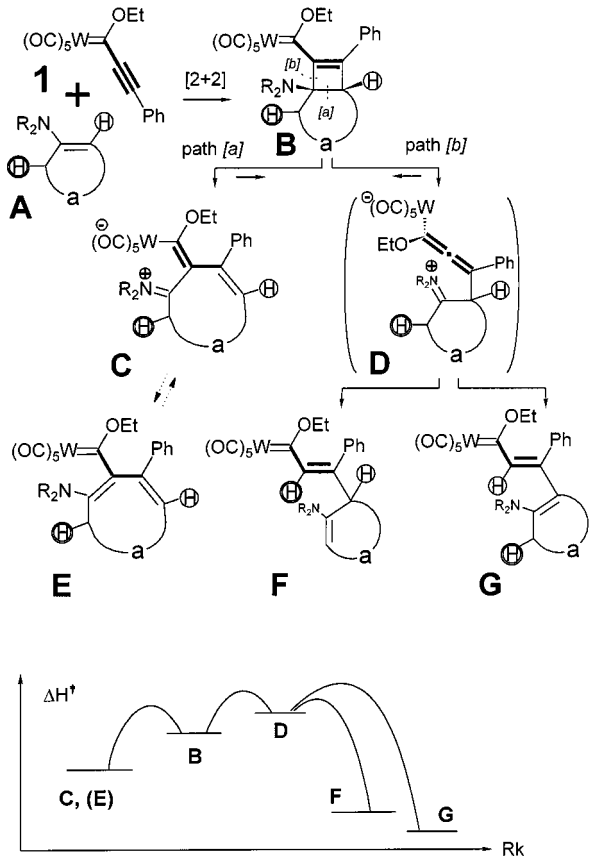


Scheme 1. Different reaction modes, represented by paths *a* and *b*, of [(4-aminocyclobutenyl)carbene]tungsten complexes **B**, and estimated reaction profile

Whilst studying the influence of the ring-size on the reactions of 1-aminoalkenes **A**, we found that addition of 1-aminocycloheptenes (Scheme 1, a = $CH_2CH_2CH_2CH_2$) and 1-aminobenzocycloheptenes to the (1-alkynyl)carbene tungsten complex **1** resulted in the generation of (cyclonona-1,3-dien-2-yl)carbene complexes of type **E** when the reaction was performed in pentane solution. Interestingly, compounds **E** could be thermally converted into conjugated 1-tungsta-1,3,5-hexatrienes of type **G** (and fragmentation products derived therefrom),[7] thus showing the ring-opening reaction path *a* of compound **B** (Scheme 1) to be reversible. Since torsional effects associated with the ring-size were expected to have a crucial bearing on the reaction course, our studies were extended to the six-membered ring derivatives 1-aminocyclohexenes **7** and 1-aminobenzocyclohexenes **2**.

Theoretical Structures of Key Intermediates

As part of a broader study on the mechanisms of the reaction pathways discussed in Scheme 1, we have optimized the structures of key intermediates in the simplified reaction between pentacarbonyl[(ethynyl)(methoxy)carbene]tungsten complex with dimethyl(vinyl)amine (**A′**) on a hybrid density functional level of theory.[8][9]

The calculations were performed with the Gaussian program.[10] Figure 1 presents the optimized conformations of the intermediates shown in Scheme 1. We have excluded the possible formation of an unconjugated 1-tungsta-1,3,6-heptatriene **F** by leaving the vinyl group of the starting enamine unsubstituted at the α position.

The relative energies in Figure 1 fit nicely with reaction Scheme 1: Formation of the (4-aminocyclobutenyl)carbene complex **B′** is expected to be exothermic by almost 20 kcal mol^{-1}. A s-*trans* conformation of the single bond between the carbene carbon atom and the neighboring olefinic group is preferred due to steric hindrance between the pentacarbonyl and dimethylamino unit. Ring strain elongates the C3−C4 single bond of the cyclobutene ring to almost 1.60 Å.

Electrocyclic ring opening of compound **B′**, yielding the cross-conjugated compound **C/E′**, is expected to be exothermic by more than 22 kcal mol^{-1}. The latter compound has a very flat potential energy surface with regard to single-bond rotations, and several conformers are expected within a range of few kcal mol^{-1}. Substituents as well as the incorporation of the crucial bonds into cyclic fragments have a strong influence on the structure and conformational energy of these metallatrienes, because the trend to retain planarity over the single bonds is competing with the steric interactions between substituents. **C/E′** exhibits a smaller deviation from planarity within the W=C1−C2=C3(NMe_2) moiety (torsional angle: 13.4°) than indicated in the crystal structure of cross-conjugated tungstatriene **3b** (torsional angle: 48.3°, Figure 2). The pattern of bond-length alternations is in line with the suggestion that compounds **C** (as found in the crystal structure of **3b**) and **E** (in the optimized structure of **C/E′**) should be considered bond-length isomers and not resonance structures of a cross-conjugated metallatriene.

The carbiminium carbonylmetallate **D** is a stable intermediate with a relative energy in the order of the (4-aminocyclobutenyl)carbene complex. Its zwitterionic character can be established from the observation that the distance between the pentacarbonyl moiety and the terminal dimethyliminium group is as short as possible. Other conformers with longer distances between the charged termini are expected to exhibit notably higher relative energies. Since our calculations treat these molecules as isolated species in the gas phase, conformations with low dipole moments are preferred. Furthermore, the C5−N bond (1.306 Å) is shorter than expected for a 1-metalla-1,3,5-hexatriene and is therefore considered a carbon−nitrogen double bond. The NBO[11] charge of the terminal $-CH=N(CH_3)_2$ moiety amounts to +0.720 e, a value that clearly indicates the localization of the positive charge within the iminium group. The negative charge is delocalized and can be assigned mainly to the $(CO)_5W$ group (−0.337 e), thus justifying the term "carbonylmetallate".

The global minimum of the model system is the conjugated 1-tungsta-1,3,5-hexatriene **G′** with a relative energy of almost 53 kcal mol^{-1} as compared to the separated reactants. The preferred conformation is *all-trans*, in line with

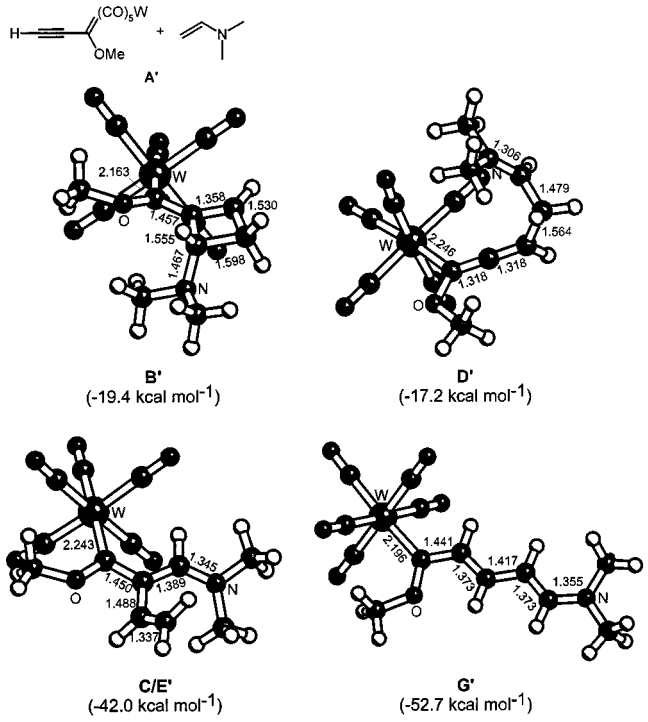


Figure 1. Optimized structures and energies of key intermediates in the reaction between pentacarbonyl[(ethynyl)(methoxy)carbene]-tungsten complex and dimethyl(vinyl)amine (A′) (energies are relative to the separated reactants; distances are given in Å)[9]

expectation for a hexatriene system. The bond lengths show typical alternation behavior in accordance with conjugative interactions.

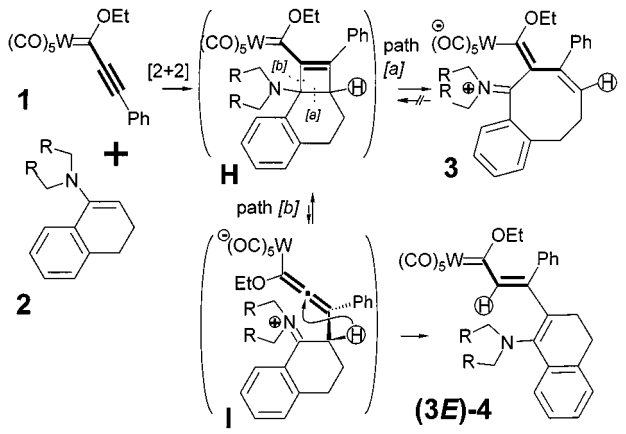
Reaction of 1-Aminobenzocyclohexenes 2 with [(1-Alkynyl)carbene]tungsten Complex 1

First of all, 1-aminobenzocyclohexenes **2a**−**c** were chosen as substrates since their reaction modes are restricted by the lack of an α-hydrogen atom with respect to the C=C(N) group. This is a prerequisite for the formation of (non-conjugated) 1-tungsta-1,3,6-heptatrienes (Scheme 1, type **F**). Reaction of 1-(dimethylamino)benzocyclohexene (**2a**) with the [(1-alkynyl)carbene]tungsten complex **1** was previously shown to produce the cyclopentadiene derivative **6a** (Scheme 3) in 80% yield when the reaction was carried out in dichloromethane.[3] The solvent was found to exert a crucial influence on the reaction course. If the reaction of compound **2a** was performed in pentane at 20°C instead of in dichloromethane, a yellow precipitate of the [(cyclooctadienyl)carbene]tungsten complex **3a** (Scheme 2, path *a*) was obtained in 52% isolated yield. The cyclopentadiene **6a** was not generated under these conditions. Similar results were obtained from reactions of 1-(diethylamino)benzocyclohexene (**2b**) and the dipropylamino derivative **2c** in pentane. Once the (cyclooctadienyl)carbene complexes **3a**−**c** had been isolated, they proved to be stable, even in solution, and did not undergo rearrangements of the type seen for the corresponding (cyclononadienyl)carbene complexes[7] mentioned above.

The second reaction course (Scheme 2, path *b*), ultimately leading to a cyclopentadiene **6a** (Scheme 3), could be unravelled, at least in part, by NMR studies. To this end, the 1-(dimethylamino)benzocyclohexene (**2a**) was added to a solution of compound **1** in CD_2Cl_2 (instead of pentane) at −55°C and ^{1}H-NMR spectra of this solution were recorded at intervals. After 5 min at −30°C, the spectrum showed mainly the signals of the starting components, but additionally featured signals due to an apparently very thermolabile compound. The latter were tentatively assigned to the (cyclobutenyl)carbene complex **H** (Scheme 2, R = H) on the basis of the following signal assignments, in particular the clearly discernible signal of the bridgehead proton: 1′-H (δ = 3.76, dd, ^3J = 1.8 Hz), 2-OCH_2 (δ = 4.70 and 4.61, each m), $N(CH_3)_2$ (δ = 2.28, s), and OCH_2CH_3 (δ = 1.49, t). Whilst these weak signals of the supposed (4-aminocyclobutenyl)carbene complex remained of essentially constant intensity, an additional set of signals resulting from the 1-tungsta-1,3,5-hexatriene (3*E*)-**4a** [3-H (δ = 7.20, s), OCH_2 (δ = 4.75 and 4.65, each m), 2 NCH_3 (δ = 2.30, s), OCH_2CH_3 (δ = 1.37, t)] gradually began to intensify. After ca. 1 h at 20°C, compound **4a** had been completely consumed and signals due to the cyclopentadiene **6a** were observed, which steadily increased in intensity. Finally, compound **6a** was identified as the major organic product of this reaction. It should be noted that no signals of the [(cyclooctadienyl)carbene]tungsten complex **3a** could be detected under these conditions.

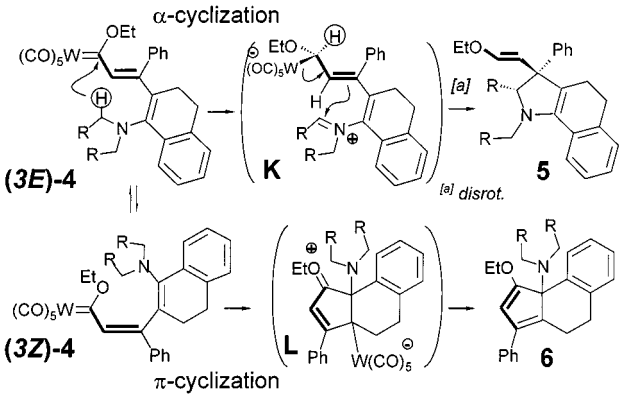
Whilst the 1-tungsta-1,3,5-hexatriene (3*E*)-**4a** could not be isolated, we succeeded in obtaining a clean sample of the corresponding diethylamino derivative (3*E*)-**4b** following the reaction of 1-(diethylamino)cyclohexene **2b** with the (1-alkynyl)carbene complex **1** by crystallization at −30°C in 43% isolated yield. The 6-(diethylamino)-1-tungsta-1,3,5-hexatriene (3*E*)-**4b** could be unambiguously characterized on the basis of its NMR data. It proved to be unstable in solution at 20°C, affording not only the expected cyclopentadiene **6b**, but also a further compound, which was identified as dihydropyrrole **5b** (Scheme 3). Clearly, compounds **5b** and **6b** are generated from 1-tungsta-1,3,5-hexatriene **4b** along the competing reaction pathways of π-cyclization and α-cyclization, respectively. In the light of earlier studies, it can be assumed that a cyclopentadiene complex **L** is generated by π-cyclization of compound (*Z*)-**4b** as precursor to the cyclopentadiene **6b** (Scheme 3).[12] A plausible reaction course leading to formation of the dihydropyrrole **5b** would involve a hydride transfer from the α-CH_2(N) group to the carbene carbon atom of compound (3*E*)-**4b** (e.g. by an antarafacial 1,7-hydrogen shift) to give intermediate **K**, which would finally undergo ring-closure (Scheme 3). Although α-cyclization reactions of this type are known for many tertiary amines,[13] only a few examples involving carbene complexes have hitherto been reported.[14]

Since an α-cyclization leading to a dihydropyrrole was not observed with the 6-(dimethylamino)-1-tungsta-1,3,5-hexatriene **4a**, but only with the diethylamino and dipro-



3,4	R	3[a]	4
a	H	52	–[b]
b	CH_3	79	43[c]
c	CH_2CH_3	74	–[b]

Scheme 2. Formation of cross-conjugated and conjugated tungstahexatrienes from (4-aminocyclobutenyl)carbene complexes **H**: [a] isolated yields in% from reactions performed in pentane; [b] compound formed but was not isolated due to its thermolability; [c] isolated yield in% from reaction performed in dichloromethane



4–6	R	5[a]	6[a]
a	H	[b]	80 (ref.[3])
b	CH_3	54	27
c	CH_2CH_3	69	–[b]

Scheme 3. α-Cyclization and π-cyclization of 6-amino-1-tungsta-1,3,5-hexatrienes **4** in dichloromethane: [a] isolated yields in% from reaction in dichloromethane; [b] compound not detected

pylamino derivatives, **4b** and **4c**, it is assumed that: (a) there is a better stabilization of the carbiminium ion center in compound **K** by the alkyl substituents R, and (b) the molecular orientation, e.g. the higher (3*E*/3*Z*) ratio enforced by steric congestion, has a crucial influence on the overall reaction course. Clearly, formation of the cyclopentadiene **6b** requires a (3*E*/3*Z*) isomerization of compound (3*E*)-**4b** in order to meet the steric requirements for the π-cyclization. On the other hand, the construction of models has shown that an "open" configuration of compound (3*E*)-**4b** should become favored over the "closed" basket-shaped configuration of the isomer (3*Z*)-**4b** if larger substituents R are introduced into the $(RCH_2)_2N$ group. Since the observed stereochemistry of compounds **5b**,**c** could result from disrotatory ring-closure of an intermediate **K**, we assume that the α-cyclization leading to dihydropyrroles might start from a 1-tungsta-1,3,5-hexatriene precursor **4** of (3*E*) configuration.[15] It is interesting to note that the "molecular switch" of the reactions shown in Scheme 3 is based on the molecular orientation induced by the various amino substituents.

Structures of (Cyclooctadienyl)carbene Complexes 3, 1-Tungsta-1,3,5-hexatrienes 4, Dihydropyrroles 5, and Cyclopentadienes 6

The structures of compounds **3a**–**c** were assigned on the basis of ^1J(C,H) and $^{2,3}J$(C,H) correlation NMR experiments. Compounds **3** are highly polarized and exhibit carbiminium carbonyltungstate structures $[^-(OC)_5W{-}C(OEt){=}C(\sim){-}C(\sim){=}N^+(CH_2R)_2]$, as is indicated by the high-field shift of the ^{13}C-NMR signal of the W,C unit (**3b**: δ = 256.0) and the low-field shift of the $C{=}N^+$ group (**3b**: δ = 169.3).[6] The zwitterionic character of compound **3b** has also been established by a crystal structure analysis (Figure 2), which revealed a pattern of alternating bond lengths [W–C1 2.287(8), C1–C2 1.408(13), C2–C3 1.464(13), C3–N31 1.337(12) Å] and a strong distortion of the W–C1=C2–C3=N31 unit from planarity [W–C1–C2–C3 –173.4(7), C1–C2–C3–N31 48.3(14)°].

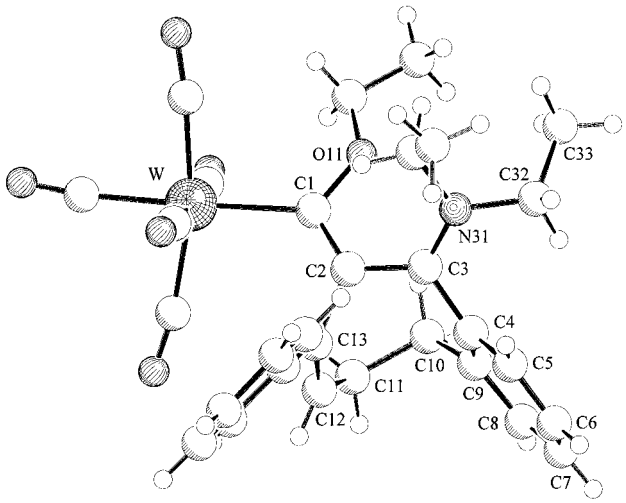


Figure 2. Crystal structure analysis of the cross-conjugated tungstatriene **3b**; selected bond lengths [Å], bond angles [°], and dihedral angles [°]: W–C1 2.287(8), C1–C2 1.408(13), C2–C3 1.464(13), C2–C13 1.482(13), C3–N31 1.337(12), C3–C4 1.490(14), C4–C9 1.38(2), C9–C10 1.50(2), C10–C11 1.55(2), C11–C12 1.49(2), C12–C13 1.334(14); C2–C1–W 125.0(6), C1–C2–C3 123.0(8), C1–C2–C13 121.9(8), C3–C2–C13 113.6(8), N31–C3–C2 123.2(9), N31–C3–C4 118.1(9), C2–C3–C4 118.7(8), C9–C4–C5 119.6(9), C9–C4–C3 121.2(9), C4–C9–C10 121.3(9), C9–C10–C11 111.3(8), C12–C11–C10 115.2(9), C13–C12–C11 127.9(10), C12–C13–C2 120.9(9); W–C1–C2–C3 –173.4(7), W–C1–C2–C13 21.7(13), C1–C2–C3–N31 48.3(14), C13–C2–C3–N31 –145.6(9), C1–C2–C3–C4 –134.0(10), C13–C2–C3–C4 32.2(12), N31–C3–C4–C9 –129.5(10), C2–C3–C4–C9 52.6(13), C3–C4–C9–C10 –5.8(14), C4–C9–C10–C11 –88.0(12), C9–C10–C11–C12 41.0(14), C10–C11–C12–C13 42.9(16), C11–C12–C13–C2 –2.3(16)

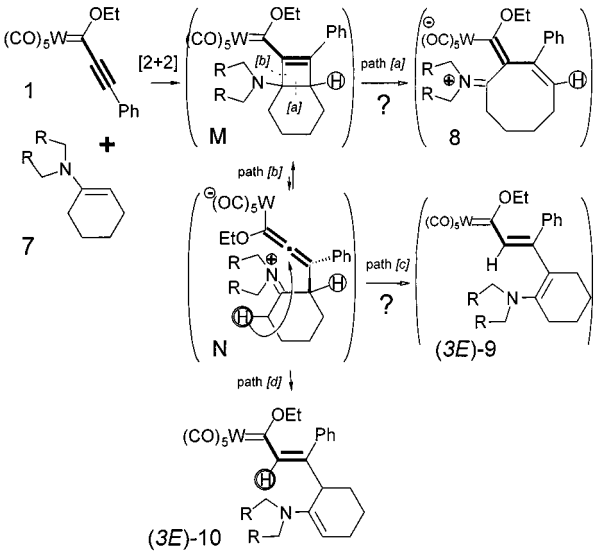
The (conjugated) 1-tungsta-1,3,5-hexatriene **4b** was characterized by its ^{1}H- and ^{13}C-NMR spectra, which showed the expected signals for W=C (δ = 301.2), C3 (δ = 142.7), and the diastereotopic OCH_2 group (δ = 4.83 and 4.70). Compounds **5b**,**c** were analysed by ^1J(C,H)- and $^{2,3}J$(C,H)-NMR correlation experiments and were identified from the signal patterns of the $NCHCH_3$ group (2-H: δ = 3.55, q, ^3J = 6.7 Hz; 2-CH_3: δ = 0.84, d, ^3J = 6.7 Hz) and the $NCHCH_2CH_3$ group (2-H: δ = 3.55, dd; 2-CH_2: δ = 1.39, m), respectively, as well as from the signals of C2 (**5b**: δ = 70.7; **5c**: δ = 78.5) and C3 (**5b**: δ = 58.7; **5c**: δ = 58.5). The configurational assignment of compounds **5b**,**c** is based on NOE measurements, where a signal enhancement was observed between the 2-CH_3 and the 3-Ph group, as well as between 2-H and the vinyl protons. The *syn* configuration of the ring is assumed to result from a disrotatory ring-closure of precursor **K** (Scheme 3). Features characteristic of the cyclopentadienes **6a**,**b** are the signals due to 2-H (**6a**: δ = 5.30;[3] **6b**: δ = 5.35) and C2 (**6a**: δ = 102.1;[3] **6b**: δ = 99.4), as well as the ν(C=C) frequency in the IR spectrum (**6a**: 1573 cm^{-1}; **6b**: 1584 cm^{-1}).

(Non-Conjugated) 1-Tungsta-1,3,6-heptatrienes 10 from 1-Aminocyclohexenes 7a−c and (1-Alkynyl)carbene Complex 1

It had been anticipated that the reactions of 1-aminocyclohexenes **7a**−**c** with the (1-alkynyl)carbene complex **1** might follow a different course from that seen with 1-aminobenzocyclohexenes **2a**−**c** due to the presence of an α-CH_2(N)= group, which, besides compounds of types **E** and **G**, could also give rise to the formation of (non-conjugated) 1-tungsta-1,3,6-heptatrienes of type **F** (Scheme 1). Compound (*E*)-**10a** was the first (non-conjugated) 6-amino-1-tungsta-1,3,6-heptatriene ever to be documented. It was detected in the reaction mixture generated from compound **7a** and the (1-alkynyl)carbene complex **1** in $CDCl_3$ through its NMR signals [*H*C=C(N) (δ = 4.95, t, ^3J = 3.8 Hz), W=*C* (δ = 313.3), and three *C*H groups (C3: δ = 147.9, C5: δ = 44.2, C7: δ = 103.7).[3] Compounds (*E*)-**10b**,**c** were obtained in an analogous manner from 1-aminocyclohexenes **7b**,**c**. Their structural assignment was based on ^{1}H-NMR, ^{13}C-NMR, and DEPT spectra, as well as ^1J(C,H), $^{2,3}J$(C,H), and *J*(H,H) correlation experiments. An NOE enhancement was observed between the protons of the OCH_2 group and the *ortho*-protons of the phenyl group, in line with the (3*E*) configuration assigned to these compounds. The presence of a non-conjugated π-system is indicated by the signals of *one* aliphatic and *two* olefinic CH groups [e.g. (3*E*)-**10b**: 3-H: δ = 7.23, C3: δ = 147.3; 6′-H: δ = 4.75, C6′: δ = 101.4; 2′-H: δ = 3.24, C2′: δ = 43.9] as well as that of the carbene carbon atom at low field [e.g. (3*E*)-**10b**: δ = 311.8]. Compounds (*E*)-**10a**−**c** proved to be less stable than the corresponding 6-alkyloxy and 6-silyloxy derivatives, which have previously been obtained from reactions of (1-alkynyl)carbene complexes with enol ethers and silyl enol ether, respectively.

π-Cyclization of Mononuclear Compounds 9 and 10

Mixtures of the 1-aminocyclohexenes **7a**−**c** with the (1-alkynyl)carbene complex **1** at −30°C give rise to NMR signals of the corresponding (non-conjugated) 1-tungsta-1,3,6-heptatrienes (3*E*)-**10** as the major products (Scheme 4). It is assumed that these compounds are generated in an "ene"-type reaction (Scheme 4, path *d*) from the precursor **N**, and that this process is faster than the formation of (conjugated) (3*E*)-1-tungsta-1,3,5-hexatrienes **9** from the same precursor (path *c*). Cross-conjugated tungstatrienes **8** could not be detected in the reaction mixtures.

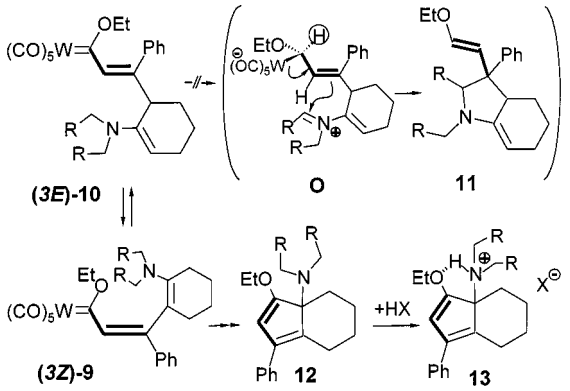


7−10	R	8	(3*E*)-10
a	H	—[a]	[b]
b	CH_3	—[a]	[b]
c	CH_2CH_3	—[a]	[b]

Scheme 4. (Non-conjugated) 1-tungsta-1,3,6-heptatrienes **10** as major products from addition of 1-aminocyclohexenes **7** to (1-alkynyl)-carbene complex **1**: [a] compound not found; [b] compound not isolated but characterized by NMR spectra

(Non-conjugated) 1-tungsta-1,3,6-heptatrienes (3*E*)-**10** are apparently generated under kinetic control and subsequently isomerize by (a supposedly catalyzed) 1,3-hydrogen transfer to (conjugated) 1-tungsta-1,3,5-hexatrienes (3*Z*)-**9**. The latter compounds do not accumulate in the reaction mixture, but slowly undergo π-cyclization to give cyclopentadienes **12** (Scheme 5).[12] In contrast to the formation of dihydropyrroles **5** from (conjugated) 1-tungsta-1,3,5-hexatrienes (3*E*)-**4** (Scheme 3), the formation of tetrahydropyrroles **11** from (non-conjugated) 1-tungsta-1,3,6-heptatrienes (3*E*)-**10** is not observed in this reaction (Scheme 5). It would appear that the formation of a non-conjugated zwitterion **O** in the first step of such reaction is likely to be less favorable than the formation of the conjugated zwitterion **K** (Scheme 3).

It should be noted that when the reactions of 1-aminocyclohexenes **7** with the (1-alkynyl)carbene complex **1** were performed in chloroform, cyclopentadienes **12** were not obtained, but protonated cyclopentadienes **13** were formed in-



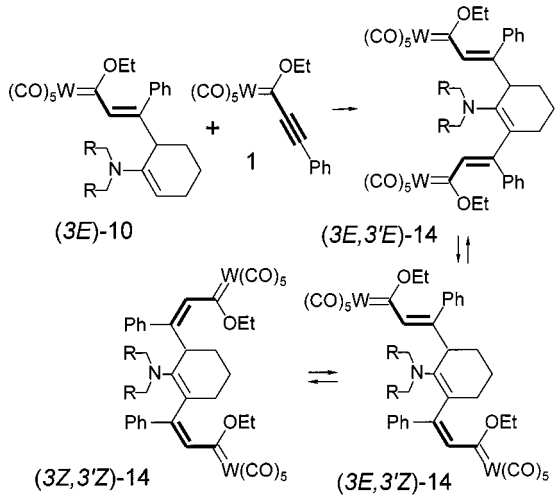
9–13	R	(3*E*)-**10**	**12**[a]	**13**
a	H	[b]	94 (ref.[3])	[b]
b	CH_3	[b]	73	[b]
c	CH_2CH_3	[b]	68	[b]

Scheme 5. π-Cyclization of (non-conjugated) 1-tungsta-1,3,6-heptatrienes **10**: [a] isolated yields in%; [b] characterized by NMR spectra

stead. Cyclopentadienes **12** could thus be generated by treatment of compounds **13** with $NaOH/H_2O$ in diethyl ether solution. The process leading to compounds **13** involves a protonation step, but the nature of the counterion X^- has yet to be established. The cyclopentadienes **12** and **13** were identified by their NMR spectral data, specifically the results of ^1J(C,H), $^{2,3}J$(C,H), and J(H,H) correlation experiments. A coupling of ^4J(H,H) = 4.9 Hz is observed between the protons of the N^+H (**13a**: δ = 11.40) and the $N^+(CH_3)_2$ groups (**13a**: δ = 3.04 and 2.66, each d). The downfield shift of the N^+H proton signal is in line with the assumption of an $N^+H\cdots O$ hydrogen bond. Compounds **13** could be unambiguously identified through their NMR spectra, but were not isolated.

Formation and Cyclization of Dinuclear Compounds 14

The type of product generated from 1-aminocyclohexenes **7a–c** and the (1-alkynyl)carbene complex **1** is found to be very much dependent on the reaction conditions. If a solution of the (1-alkynyl)carbene complex **1** in dichloromethane is slowly added to one equivalent of compound **7a–c** under vigorous stirring, (non-conjugated) 1-tungsta-1,3,6-heptatrienes (3*E*)-**10** are smoothly produced and are finally converted into cyclopentadienes **12a–c** (Scheme 4). In order to obtain good chemical yields of compounds **12**, it is important that the reaction conditions are carefully controlled. For example, if the order in which the reactants are mixed is reversed, the reaction is found to take a different course. In the presence of even a local excess of the (1-alkynyl)carbene complex **1**, 2:1 adducts are formed since the initially generated (non-conjugated) 1-tungsta-1,3,6-heptatriene (3*E*)-**10** readily adds another molecule of the (1-alkynyl)carbene complex **1** at its enamine unit to give a dinuclear compound **14** (Scheme 6). It has been unequivocally shown by NMR experiments that compounds **14** are generated from mononuclear precursors (3*E*)-**10**. The second step, i.e. the formation of a dinuclear compound, appears to be somewhat slower than formation of its mononuclear precursors. Thus, it is possible to control the reaction to give either cyclopentadienes **12** or dinuclear compounds **14** as the only products by changing the order in which the reactants are brought together.

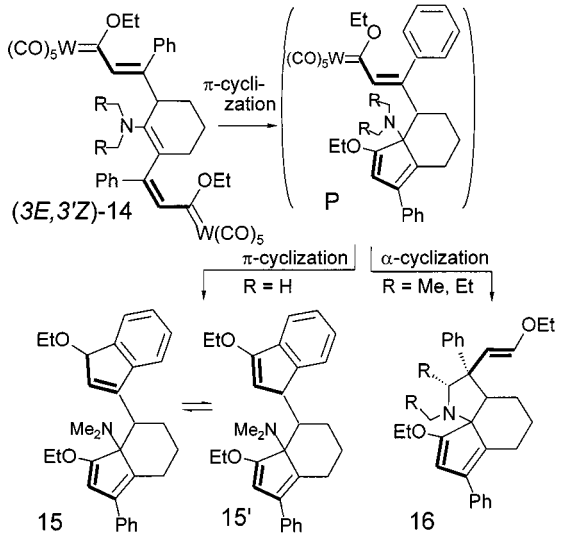


10,**14**	R	(3*E*)-**10**	(3*E*,3′*E*)-**14**	(3*E*,3′*Z*)-**14**	(3*Z*,3′*Z*)-**14**	**14**[a]
a	H	[b]	6	4	3	62
b	CH_3	[b]	1	2	0	44
c	CH_2CH_3	[b]	7	10	0	36

Scheme 6. Dimetalation of (non-conjugated) 1-tungsta-1,3,6-heptatrienes (3*E*)-**10**: [a] isolated yields in%; [b] characterized by NMR spectra; not isolated

Compounds **14a–c** were isolated by crystallization from pentane at −40°C in 36–62% yields and were characterized at −30°C (**14a**,**c**) and −70°C (**14b**) by their ^{1}H-NMR, ^{13}C-NMR, and DEPT spectra, as well as by ^1J(C,H), $^{2,3}J$(C,H), and J(H,H) correlation experiments. A set of typical signals are those due to 3-H, 3′-H, and 6-H [e.g. (3*E*,3′*Z*)-**14c**: 3-H: δ = 6.84; 3′-H: δ = 7.76, 6-H: δ = 3.42], as well as the carbene carbon atoms of the conjugated and non-conjugated 1-tungstatriene unit [e.g. (3*E*,3′*Z*)-**14c**: δ = 297.3 and 313.8, respectively]. The protons of the cyclohexene units could be assigned by TOCSY experiments. Compounds **14** form mixtures of (*E*/*Z*) isomers in solution, the ratio of which is markedly influenced by the size of the $N(CH_2R)_2$ group (Scheme 6). A "closed", basket-shaped isomer (3*Z*,3′*Z*)-**14** is generated only in the case of R = H, whereas "semi-open" isomers (3*E*,3′*Z*)-**14** and "fully-open" isomers (3*E*,3′*E*)-**14** are obtained for R = CH_3 and R = CH_2CH_3. The assignment of the (3*Z*) configuration is based on typical shift differences seen for the OCH_2 groups [e.g. (3*E*,3′*Z*)-**14c**: 2-OCH_2 for (3*E*): δ = 5.19 and 5.04; 2′-OCH_2 for (3*Z*): δ = 4.50 and 4.29], as well as on the NOE enhancement observed between 3-H and the *o*-H of the 4-Ph group. A rapid interconversion between the isomers in solution was detected by spin-saturation-transfer experi-

ments between the 3-H/3′-H protons and 2-OCH_2/2′-OCH_2 groups.



14−16	R	15	15′	16
a	H	38[a]	35[a]	−[b]
b	CH_3	−[b]	−[b]	69[a]
c	CH_2CH_3	−[b]	−[b]	75[a]

Scheme 7. Indenes and *spiro*-tetrahydropyrroles by cyclization of dinuclear complexes **14**: [a] isolated yields in%; [b] compound not observed

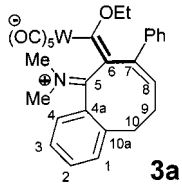
Compounds **14a**−**c** are thermolabile and undergo cyclization reactions at 20°C within 14 h by loss of both metal units. Different products are obtained depending on the size of the substituent R. Whilst indenes **15** and **15′** were generated from compound **14a** (by two successive π-cyclizations), only tricyclic *spiro*-tetrahydropyrroles **16** were obtained from compounds **14b**,**c** (by both a π-cyclization and a α-cyclization) (Scheme 7). We assume that both reaction paths are initiated by π-cyclization of the (3*Z*)-1-tungsta-1,3,5-hexatriene unit of a "semi-open" isomer (3*E*,3′*Z*)-**14a**−**c** to give first a cyclopentadiene derivative **P**, from which indenes **15** and **15′** [18] could be obtained by π-cyclization and the tricyclic *spiro*-tetrahydropyrroles **16** by α-cyclization. An α-cyclization involving a carbiminium precursor of type **O** (Scheme 5) could be enhanced by the stabilizing effect of alkyl substituents R = CH_3, CH_2CH_3.

Compounds **15** and **16** were identified by their ^{1}H-NMR, ^{13}C-NMR, and DEPT spectra, as well as by ^1J(C,H), $^{2,3}J$(C,H), and J(H,H) correlation experiments. The protons of the cyclohexene ring could be identified by TOCSY and homo-decoupling experiments. Typical of the cyclopentadiene units in compounds **15** and **15′** are the NMR signals of 2′-H and C3 (**15**: δ_H = 5.31, δ_C = 102.2; **15′**: δ_H = 5.42, δ_C = 100.6). The isomers **15** and **15′** are readily distinguished by the signals of 3-H, C3, and C1 [**15**: δ_H = 5.08 (^3J = 1.6 Hz), δ_C = 82.5 and 149.7; **15′**: δ_H = 4.55, δ_C = 157.3 and 45.9]. The structural element $NCHCH_3$ is typically observed for the *spiro*-tetrahydropyrroles **16b** (2-H: δ = 3.75, q, ^3J = 6.9 Hz; 2-CH_3: δ = 1.23, d, ^3J = 6.9 Hz; C2: δ = 68.6; C3: δ = 53.4), while an $NCHCH_2CH_3$ group is seen for compound **16c** (2-H: δ = 3.52; 2-CH_2: δ = 1.77 and 1.68; C2: δ = 76.6).

Experimental Section

All operations were performed under argon. Dried solvents were used in all experiments. − Melting points are uncorrected. − ^{1}H- and ^{13}C-NMR spectra were obtained with Bruker ARX 300, Bruker AM 360, and Varian U 600 spectrometers; multiplicities were determined by DEPT. Chemical shifts are referenced to TMS (δ = 0.00); ^{13}C shifts were assigned on the basis of ^1J(CH) and $^{2,3}J$(CH) correlation experiments. Low-temperature NMR measurements were carried out with a Bruker AM 360 instrument. − Diffractometer: Enraf-Nonius MACH III or Enraf-Nonius CAD4 with sealed tubes. − IR: Digilab FTS 45. − MS: Finnigan MAT 312. − Elemental analyses: Perkin−Elmer 240 elemental analyzer. − TLC: Merck DC-Alufolien Kieselgel 60 F254. R_f values refer to TLC tests. Column chromatographic purifications were performed on Merck Kieselgel 100.

Pentacarbonyl[(5-dimethylazonia-7-phenyl-9,10-dihydrobenzocycloocten-6-ylidene)ethyloxymethylenyl]tungstate (3a) and (1-Ethyloxy-3-phenyl-4,5-dihydrocyclopenta[*a*]naphthalen-9b−yl)-dimethylamine (6a): In a 5-mL screw-top vessel, a mixture of pentacarbonyl(1-ethyloxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1**)[2][19] (482 mg, 1.00 mmol) and dimethyl(3,4-dihydronaphthalen-1-yl)amine (**2a**)[3][20] (173 mg, 1.00 mmol) in *n*-pentane (4 mL) was stirred at 0°C for 14 h. A precipitate of compound **3a** [341 mg, 52%, R_f = 0.6 (pentane/diethyl ether, 1:1), orange crystals, dec. 91°C] was deposited, which was collected by centrifugation and washed with pentane (4 × 1 mL). Reaction of the (1-alkynyl)carbene complex **1** (482 mg, 1.00 mmol) with compound **2a** (173 mg, 1.00 mmol) in dichloromethane (instead of pentane) afforded the cyclopentadiene derivative **6a** (see ref.[3]).



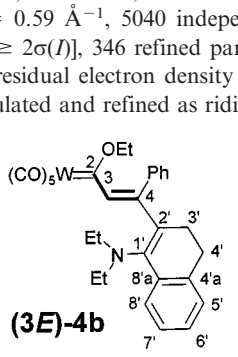
3a: ^{1}H NMR ($CDCl_3$): δ = 7.20−6.99 (m, 9 H, C_6H_4 and Ph), 5.71 (dd, 1 H, ^3J = 7.5 Hz, 8-H), 4.61 (m, 2 H, diastereotopic OCH_2), 3.11 and 2.67 (2 m, 1 H each, 10-H_2), 3.08 (br. s, 6 H, 2 NCH_3), 2.56 and 2.35 (2 m, 1 H each, 9-H_2), 1.38 (t, 3 H, OCH_2CH_3). − ^{13}C NMR ($CDCl_3$): δ = 243.2 (W=C), 203.7 and 200.3 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 170.7 (C_q, C5), 145.8, 144.1, 142.1, 135.6 and 130.2 (each C_q, C6, C7, C4a, C10a, and *i*-C Ph), 132.4 (CH, C8), 131.6, 128.7, 128.6, 127.2, 126.6 and 126.1 (1:2:2:1:1:1:1, each CH, Ph and C1−C4), 74.5 (OCH_2), 46.0 (2 NCH_3), 31.9 and 29.4 (each CH_2, C9 and C10), 16.8 (OCH_2CH_3). − IR (diffuse reflection): $\tilde{\nu}$ = 2852.1, 2055.7, 1927.4 cm^{-1}. − IR (hexane): $\tilde{\nu}$ (%) = 2055.7 (22), 1927.2 cm^{-1} (100) [ν(C≡O)]. − MS (70 eV): ^{184}W, *m/z* (%): 655 (0) [M^+], 627 (18) [M^+ − 1 CO], 515 (20) [M^+ − 5 CO], 331 (5) [M^+ − $W(CO)_5$], 71 (100), period − $C_{28}H_{25}NO_6W$ (655.4): calcd. C 51.32, H 3.84, N 2.14; found C 51.84, H 3.90, N 2.38.

6a: See ref.[3]

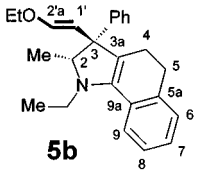
Pentacarbonyl[(5-diethylazonia-7-phenyl-9,10-dihydrobenzocycloocten-6-ylidene)ethyloxymethylenyl]tungstate (3b), (3*E*)-1,1,1,1,1-Pentacarbonyl-4-[(1-diethylamino-3,4-dihydronaphthalen-

2-yl)]-2-ethyloxy-4-phenyl-1-tungsta-1,3-butadiene (4b), 3-(2-Ethyloxyethenyl)-1-ethyl-2-methyl-3-phenyl-2,3,4,5-tetrahydro-1*H*-benzo[*g*]indole (5b), and (1-Ethyloxy-3-phenyl-4,5-dihydrocyclopenta[*a*]naphthalen-9b-yl)diethylamine (6b): Pentacarbonyl(1-ethyloxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1**) (482 mg, 1.00 mmol) and diethyl(3,4-dihydronaphthalen-1-yl)amine[20] (**2b**) (201 mg, 1.00 mmol) were treated as described above in *n*-pentane solution to give compound **3b** [red crystals from *n*-pentane/diethyl ether, 4:1, at −15°C; 540 mg, 79%, R_f = 0.5 (*n*-pentane/diethyl ether, 1:1, on silica), dec. 98°C]. Dropwise addition of a solution of compound **1** (121 mg, 0.25 mmol) in 1 mL of diethyl ether to a solution of compound **2b** (50 mg, 0.25 mmol) in 3 mL of *n*-pentane at 20°C resulted in a color change from brown to purple within a few min., during which time compound **1** was completely consumed (fast TLC analysis). The purple solution thus obtained was immediately cooled to −15°C to afford purple crystals of compound (3*E*)-**4b** [73 mg, 43%, R_f = 0.9 (pentane/diethyl ether, 1:1), dec. 111°C]. A solution of compound **1** (482 mg, 1.00 mmol) in 4 mL of dichloromethane was added to compound **2b** (201 mg, 1.00 mmol) with rapid stirring at 20°C and the mixture was subsequently stirred for 14 h at this temperature. Chromatography of the resulting mixture on alumina afforded compound **5b** [194 mg, 54%, R_f = 0.9 (pentane/diethyl ether, 1:1), yellow oil] and compound **6b** [97 mg, 27%, R_f = 0.8 (*n*-pentane/diethyl ether, 10:1), pale-yellow oil].

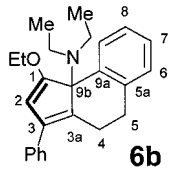
3b: ^{1}H NMR ($CDCl_3$): δ = 7.36−7.06 (m, 9 H, C_6H_4 and Ph), 5.81 (pseudo t, 1 H, 8-H), 4.81 (m, 2 H, diastereotopic OCH_2), 3.62 and 3.51 (2 br. m, 2 H each, 2 diastereotopic NCH_2), 3.22 and 2.79 (2 m, 1 H each, 10-H_2), 2.68 and 2.43 (2 m, 1 H each, 9-H_2), 1.49 (t, 3 H, OCH_2CH_3), 1.24 (br. t, 6 H, 2 NCH_2CH_3). − ^{13}C NMR ($CDCl_3$): δ = 256.0 (W=C, br.), 203.0 and 199.5 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 169.3 (C_q, C5), 145.2, 143.3, 141.7, 135.2 and 128.1 (each C_q, C6, C7, C4a, C10a, and *i*-C Ph), 132.0 (CH, C8), 129.3, 128.0, 126.5, 126.2 and 125.4 (1:3:2:1:2, each CH, Ph and C1−C4), 74.4 (OCH_2), 47.8 (2 NCH_2, br.), 31.0 and 28.7 (each CH_2, br., C9 and C10), 16.6 (OCH_2CH_3), 13.3 (2 NCH_2CH_3, br.). − IR (diffuse reflection): $\tilde{\nu}$ = 2051.5, 1897.9 cm^{-1}, period − IR (hexane): $\tilde{\nu}$ (%) = 2055.5 (22), 1916.9 cm^{-1} (100) [ν(C≡O)]. − MS (70 eV): ^{184}W, *m*/*z* (%): 683 (1) [M^+], 655 (18) [M^+ − 1 CO], 515 (20) [M^+ − 5 CO], 359 (78) [M^+ − $W(CO)_5$], 287 (100). − $C_{30}H_{29}NO_6W$ (683.4): calcd. C 52.73, H 4.28, N 2.05; found C 53.15, H 4.46, N 2.14. − X-ray crystal structure analysis of compound **3b** : Formula $C_{30}H_{29}NO_6W$, M_r = 683.39, a red crystal of dimensions 0.30 × 0.20 × 0.20 mm was selected, *a* = 10.005(2), *b* = 12.741(2), *c* = 22.708(4) Å, β = 98.09(2)°, *V* = 2865.9(9) Å^3, $\rho_{calcd.}$ = 1.584 g cm^{-3}, *F*(000) = 1352 e, μ = 40.72 cm^{-1}, empirical absorption correction using φ scan data (0.970 ≤ *C* ≤ 0.999), *Z* = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, *T* = 293 K, ω/2θ scans, 5179 reflections collected (±*h*, −*k*, −*l*), [(sinθ)/λ] = 0.59 Å^{-1}, 5040 independent and 3403 observed reflections [$I \geq 2\sigma(I)$], 346 refined parameters, *R* = 0.057, wR^2 = 0.143, max. residual electron density 2.47 (−1.92) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.[21]



(3*E*)-4b: ^{1}H NMR ($CDCl_3$, 243 K): δ = 7.60−7.22 (m, 9 H, C_6H_4 and Ph), 7.33 (s, 1 H, 3-H), 4.83 and 4.70 (2 m, 1 H each, diastereotopic OCH_2), 3.11, 2.64, 2.04 and 0.87 (4 m, 1 H each, 3′-H_2 and 4′-H_2), 2.84 and 2.72 (2 m, 2 H each, 2 NCH_2), 1.33 (t, 3 H, OCH_2CH_3), 0.51 (br. "s", 6 H, 2 NCH_2CH_3). − ^{13}C NMR ($CDCl_3$, 243 K): δ = 301.2 (W=C), 204.5 and 197.8 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 151.1, 148.3, 143.5, 139.8 and 133.7 (each C_q, C1′, C4, C4a′, C8a′, *i*-C Ph), 142.7 (CH, C3), 129.5, 128.6, 128.2, 127.5, 127.4, 126.0 and 125.4 (1:2:2:1:1:1:1, each CH, Ph and C5′−C8′), 126.3 (C_q, C2′), 78.7 (OCH_2), 44.4 (2 NCH_2, br.), 31.9 and 28.5 (each CH_2, C3′ and C4′), 14.8 (OCH_2CH_3), 12.7 (2 NCH_2CH_3, br.). − IR (diffuse reflection): $\tilde{\nu}$ = 2932.8, 2060.5, 1939.1 cm^{-1}. − IR (hexane): $\tilde{\nu}$ (%) = 2063.4 (24), 1941.4 cm^{-1} (100) [ν(C≡O)].



5b: ^{1}H NMR ($CDCl_3$): δ = 7.39−7.10 (m, 9 H, C_6H_4 and Ph), 6.41 (d, 1 H, ^3J = 13 Hz, 2′-H), 5.43 (d, 1 H, ^3J = 13 Hz, 1′-H), 3.86 (q, 2 H, OCH_2), 3.55 (q, 1 H, ^3J = 6.7 Hz, 2-H), 3.19 (m, 2 H, diastereotopic NCH_2), 2.79 (m, 2 H, diastereotopic 5-H_2), 2.03 (m, 2 H, diastereotopic 4-H_2), 1.34 (t, 3 H, OCH_2CH_3), 1.02 (t, 3 H, NCH_2CH_3), 0.84 (d, 3 H, ^3J = 6.7 Hz, 2-CH_3). − ^{13}C NMR ($CDCl_3$): δ = 147.8 (CH, C2′), 144.7 (C_q, C9b), 141.5 (C_q, *i*-C Ph), 137.5 (C_q, C5a), 130.3 (C_q, C9a), 128.8, 127.8, 127.6, 126.5, 121.8 and (3:3:1:1:1, each CH, Ph and C6−C9), 124.1 (C_q, C3a), 110.6 (CH, C1′), 70.7 (CH, C2), 65.2 (OCH_2), 58.1 (C_q, C3), 44.5 (NCH_2), 29.8 (CH_2, C5), 21.4 (CH_2, C4), 16.8 (CH_3, 2-CH_3), 14.9 (OCH_2CH_3), 12.0 (NCH_2CH_3). − IR (diffuse reflection): $\tilde{\nu}$ = 2931.1, 1696.5, 1647.3, 1447.2 cm^{-1}. − MS (70 eV), *m*/*z* (%): 359 (100) [M^+]. − $C_{25}H_{29}NO$ (359.5): calcd. C 83.52, H 8.14, N 3.90; found C 83.11, H 8.56, N 3.79.



6b: ^{1}H NMR ($CDCl_3$): δ = 7.52−7.01 (m, 9 H, Ph and C_6H_4), 5.35 (s, 1 H, 2-H), 3.99 (m, 2 H, diastereotopic OCH_2), 3.72 and 2.63 (2 m, 1 H each, 4-H_2), 2.97 and 2.63 (2 m, 1 H each, 5-H_2), 2.63 and 2.49 (2 m, 2 H each, 2 diastereotopic NCH_2), 1.42 (t, 3 H, OCH_2CH_3), 0.75 (t, 6 H, 2 NCH_2CH_3). − ^{13}C NMR ($CDCl_3$): δ = 168.6 (C_q, C1), 141.3, 138.3, 136.9, 134.4, and 134.0 (each C_q, C3, C3a, C5a, C9a, and *i*-C Ph), 128.0, 127.5, 127.3, 127.1, 126.3, and 125.4 (2:2:2:1:1:1, each CH, Ph and C6−C9), 99.4 (CH, C2), 77.6 (C_q, C9b), 65.0 (OCH_2), 44.4 (2 NCH_2), 29.7 (CH_2, C4), 23.8 (CH_2, C5), 16.2 (2 NCH_2CH_3), 15.0 (OCH_2CH_3), period − IR (diffuse reflection): $\tilde{\nu}$ = 2925.0, 1584.1 cm^{-1}, period − MS (70 eV), *m*/*z* (%): 359 (100) [M^+].

Pentacarbonyl[(5-dipropylazonia-7-phenyl-9,10-dihydrobenzocycloocten-6-ylidene)-ethyloxymethylenyl]tungstate (3c), 2-Dipropylamino-7-phenyl-9,10-dihydrobenzocycloocten-6-carbaldehyde (3′c) and 3-(2-Ethyloxyethenyl)-2-ethyl-3-phenyl-1-propyl-2,3,4,5-tetrahydro-1*H*-benzo[*g*]indole (5c): Pentacarbonyl(1-ethyloxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1**) (482 mg, 1.00 mmol) and (3,4-dihydronaphthalen-1-yl)dipropylamine (**2c**)[20] (229 mg, 1.00 mmol) were treated in *n*-pentane as described above to give

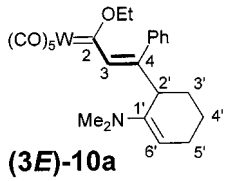
compound **3c** [red crystals from *n*-pentane/diethyl ether, 4:1, at −15°C; 526 mg, 74%, R_f = 0.5 (*n*-pentane/diethyl ether, 1:1, on silica), dec. 109°C]. A solution of compound **1** (482 mg, 1.00 mmol) in 4 mL of dichloromethane was added to compound **2c** (229 mg, 1.00 mmol) under rapid stirring at 20°C. After 14 h at this temperature, chromatography of the mixture on alumina afforded compound **5c** [267 mg, 69%, R_f = 0.9 (pentane/diethyl ether, 1:1), yellow oil] and a small amount of aldehyde **3′c** [40 mg, 11%, R_f = 0.5 (*n*-pentane/diethyl ether, 1:1, on alumina), pale-yellow oil], resulting from hydrolysis of compound **3c**.[1]

3c: ^{1}H NMR ($CDCl_3$): δ = 7.32−7.01 (m, 9 H, C_6H_4 and Ph), 5.82 (pseudo t, 1 H, 8-H), 4.84 (m, 2 H, diastereotopic OCH_2), 3.49 (br. m, 4 H, 2 NCH_2), 3.22 and 2.72 (2 m, 1 H each, 10-H_2), 2.69 and 2.40 (2 m, 1 H each, 9-H_2), 1.75 (br. m, 4 H, 2 NCH_2CH_2), 1.48 (t, 3 H, OCH_2CH_3), 0.93 (br. t, 6 H, 2 $NCH_2CH_2CH_3$), period − ^{13}C NMR ($CDCl_3$): δ (W=C, not observed), 203.2 and 199.6 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 169.9 (C_q, C5), 145.6, 143.2, 141.7, 135.6, and 130.7 (each C_q, C6, C7, C4a, C10a, and *i*-C Ph), 132.1 (CH, C8), 129.4, 128.8, 128.2, 127.9, 126.5, 125.8, and 125.6 (1:1:3:1:1:1:1, each CH, Ph and C1−C4), 74.5 (OCH_2), 54.9 (2 NCH_2, br.), 31.2 and 28.8 (each CH_2, br., C9 and C10), 21.3 (2 NCH_2CH_2), 16.7 (OCH_2CH_3), 11.5 ($NCH_2CH_2CH_3$). − IR (diffuse reflection): $\tilde{\nu}$ = 2051.1, 1899.6 cm^{-1}. − IR (hexane): $\tilde{\nu}$ (%) = 2054.4 (56), 1920.6 cm^{-1} (100) [ν(C≡O)]. − MS (70 eV): ^{184}W, *m*/*z* (%): 711 (0) [M^+], 683 (1) [M^+ − 1 CO], 571 (1) [M^+ − 5 CO], 387 (14) [M^+ − $W(CO)_5$], 287 (100). − $C_{32}H_{33}NO_6W$ (711.5): calcd. C 54.02, H 4.68, N 1.97; found C 54.04, H 4.97, N 1.93.

3′c: ^{1}H NMR ($CDCl_3$): δ = 8.95 (s, 1 H, CHO), 7.31−7.05 (m, 9 H, C_6H_4 and Ph), 5.78 (pseudo t, 1 H, 8-H), 3.41 (m, 4 H, 2 NCH_2), 2.76 (m, 2 H, 10-H_2), 1.69 (m, 2 H, 9-H_2), 1.61 (br. m, 4 H, 2 NCH_2CH_2), 0.93 (t, 6 H, 2 $NCH_2CH_2CH_3$). − ^{13}C NMR ($CDCl_3$): δ = 184.1 (C_q, CHO), 144.9, 143.6, 143.1, and 136.8 (each C_q, C4a, C10a, C5, C7, and *i*-C Ph), 129.2, 128.6, 128.1, 127.9, 126.4, 126.1, and 125.9 (1:1:1:1:3:1:2, each CH, C8, Ph, and C1−C4), 115.2 (C_q, C6), 55.1 (2 NCH_2), 31.3 and 29.5 (each CH_2, C9 and C10), 21.7 (2 NCH_2CH_2), 11.4 (2 $NCH_2CH_2CH_3$). − IR (diffuse reflection): $\tilde{\nu}$ = 1628.9 cm^{-1} [ν(C=O)]. − MS (70 eV): *m*/*z* (%): 359 (100) [M^+].

5c: ^{1}H NMR ($CDCl_3$): δ = 7.49−7.34 (m, 9 H, C_6H_4 and Ph), 6.42 (d, 1 H, ^3J = 12.8 Hz, 2′-H), 5.56 (d, 1 H, ^3J = 12.8 Hz, 1′-H), 3.86 (q, 2 H, OCH_2), 3.55 (dd, 1 H, ^3J = 5.5 Hz, 2-H), 3.14 and 2.99 (2 m, 1 H each, diastereotopic NCH_2), 2.79 (m, 2 H, diastereotopic 5-H_2), 1.93 (m, 2 H, diastereotopic 4-H_2), 1.34 (t, 3 H, OCH_2CH_3), 1.39 (m, 2 H, 2-CH_2CH_3), 1.18 (m, 2 H, NCH_2CH_2), 0.83 (t, 3 H, $NCH_2CH_2CH_3$), 0.71 (t, 3 H, 2-CH_2CH_3). − ^{13}C NMR ($CDCl_3$): δ = 147.7 (CH, C2′), 144.9 (C_q, C9b), 141.8 (C_q, *i*-C Ph), 137.4 (C_q, C5a), 130.4 (C_q, C9a), 128.7, 127.6, 127.5, 126.4, 126.2, 126.0, and 121.9 (2:2:1:1:1:1:1, each CH, Ph and C6−C9), 123.8 (C_q, C3a), 111.6 (CH, C1′), 78.5 (CH, C2), 65.1 (OCH_2), 58.5 (C_q, C3), 56.2 (NCH_2), 29.7 (CH_2, C5), 25.5 and 20.0 (each CH_2, NCH_2CH_2 and 2-CH_2CH_3), 21.3 (CH_2, C4), 14.9 (OCH_2CH_3), 11.7 ($NCH_2CH_2CH_3$), 11.5 (2-CH_2CH_3). − IR (diffuse reflection): $\tilde{\nu}$ = 2931.2, 1685.6, 1650.1, 1452.7 cm^{-1}. − MS (70 eV): *m*/*z* (%): 387 (38) [M^+], 358 (100) − Exact mass (ref. 380.97601) for $C_{27}H_{33}NO$: calcd. 387.25623; found 387.25609.

(3*E*)-1,1,1,1,1-Pentacarbonyl-4-(2-dimethylaminocyclohex-2-en-1-yl)-2-ethyloxy-4-phenyl-1-tungsta-1,3-butadiene (10a), (3-Ethyloxy-1-phenyl-4,5,6,7-tetrahydroinden-3a-yl)dimethylamine (12a), (3-Ethyloxy-1-phenyl-4,5,6,7-tetrahydroinden-3a-yl)dimethylammonium Salt 13a, Dimethyl[2,6-bis(1,1,1,1,1-pentacarbonyl-2-ethyloxy-4-phenyl-1-tungsta-1,3-butadien-4-yl)cyclohex-1-enyl]amine (14a), 3-(3-Ethyloxy-3a-dimethylamino-1-phenyl-4,5,6,7-tetrahydro-3a*H*-inden-4-yl)-1-ethyloxyindene (15), and 1-(3-Ethyloxy-3a-dimethylamino-1-phenyl-4,5,6,7-tetrahydro-3a*H*-inden-4-yl)-3-ethyloxyindene (15′): Pentacarbonyl(1-ethyloxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1**) (121 mg, 0.25 mmol) in 1 mL of $CDCl_3$ was added to (cyclohex-1-enyl)dimethylamine (**7a**) (31 mg, 0.25 mmol) in an NMR tube at 0°C to give an orange solution of compound (3*E*)-**10a**. NMR spectra of this solution were recorded immediately at −30°C. A solution of compound **1** (241 mg, 0.50 mmol) in 3 mL of dichloromethane was added to compound **7a** (63 mg, 0.50 mmol) in a 3-mL screw-top vessel under stirring at 0°C. Chromatography on silica after 14 h at 20°C (column 30 × 2 cm), eluting with *n*-pentane/diethyl ether (10:1) afforded $W(CO)_6$ and (after a small amount of colored products, which were discarded) a pale-yellow fraction containing compound **12a** [133 mg, 94%, R_f = 0.9 (*n*-pentane/diethyl ether, 10:1, on silica), yellow oil].[3] When the reaction of the (1-alkynyl)carbene complex **1** with compound **7a** was performed in chloroform instead of dichloromethane, the protonated aminocyclopentadiene **13a** was obtained, from which compound **12a** could be generated by treatment with $NaOH/H_2O$. Formation of compound **13a** as the sole product required ca. 14 h at 50°C. The counterion of compound **13a** was not identified. To pentacarbonyl(1-ethyloxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1**) (241 mg, 0.50 mmol) in a 5-mL screw-top vessel, a solution of cyclohex-1-enyl-dimethylamine (**7a**) (31 mg, 0.25 mmol) in 4 mL of hexane was added with stirring at 20°C to give a blue to brownish solution. After 14 h at −40°C, a blue/black oil was obtained, which was isolated by centrifugation and washed with hexane (3 × 1 mL) to give compound **14a** [169 mg, 62%, R_f = 0.9 (*n*-pentane/diethyl ether, 10:1, on silica)]. NMR spectra were recorded at −30°C and showed that the three configurational isomers (3′′*E*,3′*E*)-**14a**, (3′′*E*,3′*Z*)-**14a**, and (3′′*Z*,3′*Z*)-**14a** were present in a 6:4:3 ratio. Reaction of compound **1** (241 mg, 0.50 mmol) with compound **7a** (31 mg, 0.25 mmol) in 4 mL of dichloromethane in a 5-mL screw-top vessel for 14 h at 20°C afforded a blue to brownish solution, from which a small amount of compound **14a** was isolated by chromatography on neutral alumina (column 30 × 1 cm) eluting with *n*-pentane/diethyl ether, 10:1, together with a pale-yellow fraction containing the indenes **15** [42 mg, 38%, R_f = 0.4 (*n*-pentane/diethyl ether, 10:1)] and **15′** [39 mg, 35%, R_f = 0.5 in *n*-pentane/diethyl ether, 10:1)].



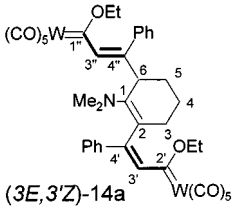
(3*E*)-10a

(3*E*)-10a: ^{1}H NMR ($CDCl_3$, 243 K, 360 MHz): δ = 7.45−7.04 (m, 7 H, Ph and 3-H), 4.88 (br. dd, 1 H, 6′-H), 4.45 and 4.33 (2 m, 1 H each, diastereotopic OCH_2), 3.30 (m, 1 H, 2′-H), 2.66 (s, 6 H, 2 NCH_3), 2.27, 2.11, and 1.58 (3 m, 1:1:4 ratio, 3′-H_2−5′-H_2), 0.74 (t, 3 H, OCH_2CH_3). − ^{13}C NMR ($CDCl_3$, 243 K, 90 MHz): δ = 309.6 (W=C), 204.4 and 198.2 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 146.74 (CH, C3), 146.70, 144.1, and 141.4 (each C_q, C1′, C4 and *i*-C Ph), 128.0, 127.1, and 126.9 (2:2:1 ratio, each CH, Ph), 102.7 (CH, C6′), 78.7 (OCH_2), 44.0 (CH, C2′), 40.9 (2 NCH_3), 25.4, 24.1, and 16.4 (each CH_2, C3′−C5′), 13.3 (OCH_2CH_3).

12a: See ref.[3]

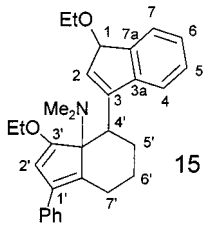
13a: ^{1}H NMR ($CDCl_3$, 30°C, 360 MHz): δ = 11.40 (br. m, 1 H, NH···O), 7.44−7.28 (m, 5 H, Ph), 5.50 (s, 1 H, 2-H), 4.02 (m, 2 H, diastereotopic OCH_2), 3.12, 2.88, 2.66, 2.29, 2.10, 1.88, 1.71, and

1.20 (8 m, 1 H each, diastereotopic 4-H_2−7-H_2), 3.04 and 2.66 (2 d, 3 H each, ^3J = 4.9 Hz, 2 NCH_3), 1.47 (t, 3 H, OCH_2CH_3).



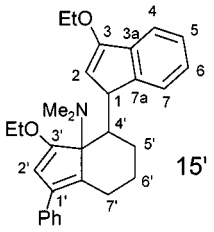
(3*E*,3′*Z*)-**14a**

14a: (3′′*E*,3′*E*)-**14a**, [(3′′*E*,3′*Z*)-**14a**] and {(3′′*Z*,3′*Z*)-**14a**}: ^{1}H NMR (CD_2Cl_2, 243 K, 600 MHz): δ = 7.46−7.03 (m, 10 H, 2 Ph), 7.01 (6.75) {7.35} (s, 1 H, 3′-H), 6.77 (7.63) {7.62} (s, 1 H, 3′′-H), 4.49 and 4.34 [5.03 and 4.92] {4.87 and 4.82} (2 m, 1 H each, diastereotopic 2′-OCH_2), 4.25 and 4.12 [4.49 and 4.34] {4.49 and 4.34} (2 m, 1 H each, diastereotopic 2′′-OCH_2), 3.62 [3.49] {3.56} (br. m, 1 H, 6-H), 2.76 [3.19] {2.59} (s, 6 H, 2 NCH_3), 2.32, 2.00, 1.78 and 1.59 (4 br. m, ratio 1:1:2:2 H, 3-H_2−5-H_2), 0.77 [1.76] (t, 3 H, 2′-OCH_2CH_3), 0.75 [0.67] (t, 3 H, 2′′-OCH_2CH_3). − ^{13}C NMR (CD_2Cl_2, 243 K, 150 MHz): δ = 311.8 [289.7] (W=C2′′), 312.8 [296.0] (W=C2′), 205.0, 204.8, 204.5, 198.9, 197.7, and 197.6 [1:1:1:4:4:4, *trans*- and *cis*-CO, 2 $W(CO)_5$], 154.2 (C_q, C4′), 152.5 (C_q, C1), 146.3 (C_q, C4′′), 147.0 [145.8] {132.2} (CH, C3′′), 145.2 (C_q, *i*-C 4′-Ph), 141.7 [140.6] {143.6} (CH, C3′), 142.5 (C_q, *i*-C 4′′-Ph), 129.5−127.2 (10 CH, 2 Ph), 120.3 (C_q, C2), 79.4 [79.5] and 77.1 [78.8] (2′′-OCH_2 and 2′-OCH_2), 47.4 [47.0] {46.5} (CH, C6), 43.5 [42.0] {43.1} (2 NCH_3), 30.0, 27.1, and 17.6 [31.7, 25.0, and 19.7] (each CH_2, C3−C5), 13.6 and 13.4 [15.7 and 13.3] {15.6 and 14.6} (2′-OCH_2CH_3 and 2′′-OCH_2CH_3). − IR (diffuse reflection): $\tilde{\nu}$ = 2061.2, 1924.2, 1911.2 cm^{-1}.



15: ^{1}H NMR ($CDCl_3$, 303 K, 360 MHz): δ = 7.38−7.05 (m, 9 H, Ph and 4-H−7-H), 6.33 (d, 1 H, ^3J = 1.6 Hz, 2-H), 5.31 (s, 1 H, 2′-H), 5.08 (d, 1 H, ^3J = 1.6 Hz, 3-H), 3.54, 3.41, and 3.28 (3 m, ratio 1:1:2 H, diastereotopic 3-OCH_2 and 3′-OCH_2); 2.81, 2.43, 2.11, 1.92, 1.68, and 1.26 (6 m, 1 H each, diastereotopic 5′-H_2−7′-H_2), 2.49 (m, 1 H, 4′-H), 2.29 (s, 6 H, 2 NCH_3), 1.12 and 0.53 (2 t, 3 H each, 3-OCH_2CH_3 and 3′-OCH_2CH_3). − ^{13}C NMR ($CDCl_3$, 303 K, 90 MHz): δ = 168.8 (C_q, C3′), 149.7 (C_q, C1), 145.6 (C_q, C7a), 143.1 (C_q, C3a), 137.1 (C_q, *i*-C Ph), 136.1 (C_q, C7a′), 133.9 (CH, C2), 131.9 (C_q, C1′); 128.2, 127.9, 127.4, 126.5, 125.1, 122.9, and 119.6 (2:2:1:1:1:1:1 CH, Ph and C4−C7), 102.2 (CH, C2′), 82.5 (CH, C3), 74.9 (C_q, C3a′), 64.1 and 61.8 (3-OCH_2 and 3′-OCH_2), 46.2 (CH, C4′), 40.6 (2 NCH_3), 27.9, 27.2, and 23.4 (each CH_2, C5′−C7′), 15.8 and 13.7 (3-OCH_2CH_3 and 3′-OCH_2CH_3). − IR (diffuse reflection): $\tilde{\nu}$ = 1586.2 cm^{-1}. − MS (70 eV): *m*/*z* (%): 441 (78) [M^+], 412 (100).

15′: ^{1}H NMR ($CDCl_3$, 303 K, 360 MHz): δ = 7.31−7.03 (m, 9 H, Ph and 4-H−7-H), 5.44 (d, 1 H, ^3J = 2.2 Hz, 2-H), 5.42 (s, 1 H, 2′-H), 4.55 (br. dd, 1 H, 1-H), 4.06 (m, 2 H, diastereotopic 3′-OCH_2), 3.94 (q, 2 H, 3-OCH_2), 2.71, 1.99, 1.63, 0.88, and 0.79 (5 m, ratio 1:1:2:1:1 H, diastereotopic 5′-H_2−7′-H_2), 1.97 (m, 1 H, 4′-H), 2.45 (s, 6 H, 2 NCH_3), 1.38 and 1.27 (2 t, 3 H each, 3-OCH_2CH_3 and 3′-OCH_2CH_3). − ^{13}C NMR ($CDCl_3$, 303 K, 90 MHz): δ = 170.1 (C_q, C3′), 157.3 (C_q, C3), 149.9 (C_q, C7a), 139.3 (C_q, C3a), 137.1 (C_q, *i*-C Ph), 136.3 and 132.5 (each C_q, C1′ and C7a′), 128.2, 128.0, 126.5, 126.0, 125.7, 122.3, and 117.7 (2:2:1:1:1:1:1 CH, Ph and C4−C7), 102.8 (CH, C2), 100.6 (CH, C2′), 75.1 (C_q, C3a′), 65.3 and 64.8 (3-OCH_2 and 3′-OCH_2), 50.4 (CH, C4′), 45.9 (CH, C1), 41.7 (2 NCH_3), 28.5, 24.5, and 24.4 (each CH_2, C5′−C7′), 14.9 and 14.7 (3-OCH_2CH_3 and 3′-OCH_2CH_3). − IR (diffuse reflection): $\tilde{\nu}$ = 2932.4, 1582.0 cm^{-1}. − MS (70 eV): *m*/*z* (%): 441 (22) [M^+], 282 (100).



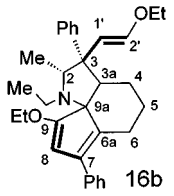
(3*E*)-1,1,1,1,1-Pentacarbonyl-4-(2-diethylaminocyclohex-2-enyl)-2-ethyloxy-4-phenyl-1-tungsta-1,3-butadiene (10b), (3-Ethyloxy-1-phenyl-4,5,6,7-tetrahydroinden-3a-yl)diethylamine (12b), (3-Ethyloxy-1-phenyl-4,5,6,7-tetrahydroinden-3a-yl)diethylammonium Salt 13b, Diethyl[2,6-bis(1,1,1,1,1-pentacarbonyl-2-ethyloxy-4-phenyl-1-tungsta-1,3-butadien-4-yl)cyclohex-1-enyl]amine (14b), and 9-Ethyloxy-3-(2-ethyloxyethenyl)-1-ethyl-2-methyl-3,7-diphenyl-2,3,3a,4,5,6-hexahydro-1*H*-1-azacyclopenta[*d*]indene (16b): Pentacarbonyl(1-ethyloxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1**) (121 mg, 0.25 mmol) in 1 mL of $CDCl_3$ was added to (cyclohex-1-enyl)diethylamine (**7b**)[20] (38 mg, 0.25 mmol) in an NMR tube at 0°C to give an orange solution of compound (3*E*)-**10b**. NMR spectra of this solution were recorded immediately at −10°C. A solution of compound **1** (482 mg, 1.00 mmol) in 3 mL of dichloromethane was added to compound **7b** (153 mg, 0.50 mmol) in a 5-mL screw-top vessel under stirring at 0°C. Chromatography on silica after 14 h at 20°C (column 30 × 2 cm), eluting with *n*-pentane/diethyl ether, 10:1, afforded $W(CO)_6$ and (after a small amount of colored products, which were discarded) a pale-yellow fraction containing compound **12b** [227 mg, 73%, R_f = 0.9 (*n*-pentane/diethyl ether, 10:1, on silica), yellow oil]. When the reaction of the (1-alkynyl)carbene complex **1** with compound **7b** was performed in chloroform instead of dichloromethane, the protonated aminocyclopentadiene **13b** was obtained, from which compound **12b** could be generated by treatment with $NaOH/H_2O$. Formation of compound **13b** as the sole product required ca. 14 h at 50°C. The counterion of compound **13b** was not identified. To pentacarbonyl(1-ethyloxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1**) (241 mg, 0.50 mmol) in a 5-mL screw-top vessel, a solution of cyclohex-1-enyl-diethylamine (**7b**) (38 mg, 0.25 mmol) in 4 mL of hexane was added with stirring at 20°C to give a blue to brownish solution. After 14 h at −40°C, black crystals of compound **14b** separated, which were isolated by centrifugation and washed with hexane [123 mg, 44%, R_f = 0.9 (*n*-pentane/diethyl ether, 10:1, on silica), dec. 77°C]. NMR spectra were recorded at −70°C and showed that the two configurational isomers (3′′*E*,3′*E*)-**14b** and (3′′*E*,3′*Z*)-**14b** were present in a 1:2 ratio. Reaction of compound **1** (241 mg, 0.50 mmol) with compound **7b** (38 mg, 0.25 mmol) in 4 mL of dichloromethane in a 5-mL screw-top vessel for 14 h at 20°C afforded a blue to brownish solution, from which a small amount of compound **14b** was isolated by chromatography on neutral alumina (column 30 × 1 cm) eluting with *n*-pentane/diethyl ether, 10:1, together with a pale-yellow fraction of *spiro*-tetrahydropyrrole **16b** [59 mg, 69%, R_f = 0.9 (*n*-pentane/diethyl ether, 10:1, on silica), yellow oil].

(3*E*)-10b: ^{1}H NMR ($CDCl_3$, 263 K, 600 MHz): δ = 7.31, 7.26, and 7.01 (3 m, ratio 2:1:2 H, Ph), 7.23 (s, 1 H, 3-H), 4.75 (dd, 1 H, ^3J = 4.4 Hz, 6′-H), 4.52 and 4.30 (2 m, 1 H each, diastereotopic OCH_2), 3.24 (m, 1 H, 2′-H), 3.21 and 2.92 (2 m, 2 H each, 2 diastereotopic NCH_2), 2.23, 2.09, 1.64, 1.57, and 1.48 (5 m, ratio 1:1:1:2:1, 3′-H_2−5′-H_2), 1.05 (t, 6 H, 2 NCH_2CH_3), 0.78 (br. t, 3 H, OCH_2CH_3). − ^{13}C NMR ($CDCl_3$, 263 K, 150 MHz): δ = 311.8 (W=C), 204.2 and 197.4 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 147.3 (CH, C3), 146.1, 141.7, and 141.2 (each C_q, C1′, C4, and *i*-C Ph), 128.6, 127.5, and 127.0 (2:2:1, CH each, Ph), 101.4 (CH, C6′), 78.7 (OCH_2), 43.9 (CH, C2′), 42.9 (2 NCH_2), 26.5, 24.7, and 17.4 (each CH_2, C3′−C5′), 13.3 (OCH_2CH_3), 12.5 (2 NCH_2CH_3).

12b: ^{1}H NMR ($CDCl_3$, 298 K, 600 MHz): δ = 7.34 and 7.21 (2 m, ratio 4:1 H, Ph), 5.18 (s, 1 H, 2-H), 3.84 (m, 2 H, OCH_2), 2.79 and 2.53 (2 m, 2 H each, 2 NCH_2), 2.75 and 2.20 (2 m, 1 H each, diastereotopic 7-H_2), 2.47 and 1.03 (2 m, 1 H each, diastereotopic 4-H_2), 1.85 and 1.16 (2 m, 1 H each, diastereotopic 5-H_2), 1.82 and 1.42 (2 m, 1 H each, diastereotopic 6-H_2), 1.34 (t, 3 H, OCH_2CH_3), 1.01 (t, 6 H, 2 NCH_2CH_3). − ^{13}C NMR ($CDCl_3$, 298 K, 150 MHz): δ = 172.9 (C_q, C3), 137.6 (C_q, *i*-C Ph), 136.3 (C_q, C7a), 131.4 (C_q, C1), 128.1, 127.9, and 126.2 (2:2:1, each CH, Ph), 97.5 (CH, C2), 72.9 (C_q, C3a), 64.7 (OCH_2), 42.7 (2 NCH_2, br.), 35.4 (CH_2, C4), 30.1 (CH_2, C5), 24.0 (CH_2, C7), 20.8 (CH_2, C6), 15.9 (2 NCH_2CH_3), 14.7 (OCH_2CH_3). − IR (diffuse reflection): $\tilde{\nu}$ = 2913.8, 1585.5 cm^{-1}. − MS (70 eV): *m*/*z* (%): 311 (50) [M^+], 282 (100).

13b: ^{1}H NMR ($CDCl_3$, 298 K, 600 MHz): δ = 10.45 (br. m, 1 H, NH···O), 7.40 and 7.36 (2 m, ratio 2:3 H, Ph), 5.47 (s, 1 H, 2-H), 3.99 (m, 2 H, diastereotopic OCH_2), 3.70, 3.59, 3.28, and 3.06 (4 m, 1 H each, 2 diastereotopic NCH_2), 3.44 and 2.86 (2 m, 1 H each, diastereotopic 7-H_2), 2.73 and 1.44 (2 m, 1 H each, diastereotopic 4-H_2), 2.57 and 1.66 (2 m, 1 H each, diastereotopic 6-H_2), 2.10 and 1.18 (2 m, 1 H each, diastereotopic 5-H_2), 1.70 and 1.43 (2 t, 3 H each, 2 NCH_2CH_3), 1.44 (t, 3 H, OCH_2CH_3). − ^{13}C NMR ($CDCl_3$, 298 K, 150 MHz): δ = 163.5 (C_q, C3), 137.8 (C_q, *i*-C Ph), 134.6 (C_q, C7a), 129.5 (C_q, C1), 128.3, 127.73, and 127.69 (2:2:1, each CH, Ph), 103.4 (CH, C2), 74.7 (C_q, C3a), 66.3 (OCH_2), 44.6 and 43.9 (2 NCH_2), 33.5 (CH_2, C4), 29.0 (CH_2, C5), 23.5 (CH_2, C7), 19.3 (CH_2, C6), 14.2 and 11.0 (2 NCH_2CH_3), 10.4 (OCH_2CH_3).

14b: (3′′*E*,3′*Z*)-**14b** [(3′′*E*,3′*E*)-**14b**]: ^{1}H NMR (CD_2Cl_2, 203 K, 600 MHz): δ = 7.43 ("d", 2 H, *o*-H 4′-Ph), 7.40 (s, 1 H, 3′-H), 7.38−6.96 (m, 8 H, 4′′-Ph and *m*- and *p*-H 4′-Ph), 6.76 (s, 1 H, 3′′-H), 5.03 and 4.85 [4.41 and 4.18] (2 m, 1 H each, diastereotopic 2′-OCH_2), 4.41 and 4.18 [4.23 and 4.08] (2 m, 1 H each, diastereotopic 2′′-OCH_2), 3.46 [3.50] (br. m, 1 H, 6-H), 2.96, 2.77, 2.69, and 2.51 (4 br. m, 1 H each, 2 diastereotopic NCH_2), 2.63, 2.04, 1.75, and 1.62 [2.62, 2.19, 1.87, 1.63, 1.50, and 1.32] (4 [6] br. m, ratio 1:1:2:2 H [1 H each], 3-H_2−5-H_2), 1.80 (t, 3 H, 2′-OCH_2CH_3), 0.78 and 0.62 (2 t, ratio 6:3 H, 2′′-OCH_2CH_3 and 2 NCH_2CH_3). − ^{13}C NMR (CD_2Cl_2, 203 K, 150 MHz): δ = 313.3 (W=C2′′), 294.4 (W=C2′), 205.4, 204.7, 198.6, and 197.7 [1:1:4:4, *trans*- and *cis*-CO, 2 $W(CO)_5$], 153.8 (C_q, C4′), 152.6 (C_q, C1), 146.8 (C_q, C4′′), 146.7 (CH, C3′′), 145.3 (C_q, *i*-C 4′-Ph), 143.7 (CH, C3′), 141.3 (C_q, *i*-C 4′′-Ph), 129.1, 128.7, 128.5, 128.2, 128.0, 127.8, and 127.7 (1:2:2:2:1:1:1, each CH, 2 Ph), 122.9 (C_q, C2), 79.6 (2′-OCH_2), 79.4 (2′′-OCH_2), 50.6 and 39.5 (each NCH_2), 46.1 (CH, C6), 32.3, 27.7, and 19.1 [30.7, 25.8, and 21.2] (each CH_2, C3−C5), 16.1 (2′-OCH_2CH_3), 14.5 (2′′-OCH_2CH_3), 13.0 and 12.0 (each NCH_2CH_3). − IR (diffuse reflection): $\tilde{\nu}$ = 2961.7, 2061.2, 1924.2, 1911.2 cm^{-1}. − IR (hexane): $\tilde{\nu}$ (%) = 2063.1 (27), 1938.4 cm^{-1} (100) [ν(C≡O)]. − MS (70 eV): ^{184}W, *m*/*z* (%): 1117 (0) [M^+], 837 (0) [M^+ − 10 CO], 469 (18) [M^+ − 2 $W(CO)_5$], 352 (100). − $C_{42}H_{39}NO_{12}W_2$ (1117.5): calcd. C 45.14, H 3.52, N 1.25; found C 44.46, H 3.20, N 1.48.



16b

16b: ^{1}H NMR ($CDCl_3$, 303 K, 360 MHz): δ = 8.07 (br. m, 2 H, *o*-H 3-Ph), 7.31 and 7.21 (2 m, 4 H each, 7-Ph and *m*-, *p*-H 3-Ph), 6.43 (d, 1 H, ^3J = 13 Hz, 2′-H), 5.20 (s, 1 H, 8-H), 5.14 (d, 1 H, ^3J = 13 Hz, 1′-H), 3.92 (m, 2 H, diastereotopic 9-OCH_2), 3.80 (q, 2 H, 2′-OCH_2), 3.75 (q, 1 H, ^3J = 6.9 Hz, 2-H), 3.11 (dd, 1 H, 3a-H), 2.64 and 2.45 (2 m, 1 H each, diastereotopic NCH_2), 2.41 and 2.24 (2 m, 1 H each, diastereotopic 6-H_2), 1.37 and 1.32 (2 t, 3 H each, 2′-OCH_2CH_3 and 9-OCH_2CH_3), 1.23 (d, 3 H, ^3J = 6.9 Hz, 2-CH_3), 1.14 (m, 2 H, 4-H_2), 1.10 (t, 3 H, NCH_2CH_3), 0.88 and −0.19 (2 m, 1 H each, diastereotopic 5-H_2). − ^{13}C NMR ($CDCl_3$, 303 K, 90 MHz): δ = 172.3 (C_q, C9), 146.2 (CH, C2′), 142.5 (C_q, *i*-C 3-Ph), 137.5 (C_q, *i*-C 7-Ph), 135.4 (C_q, C7), 134.1 (C_q, C6a), 131.7 (CH, *o*-C 3-Ph), 128.4, 127.6, 126.5, 126.3, and 125.8 (2:2:2:1:1, each CH, 7-Ph and *m*-, *p*-C 3-Ph), 113.2 (CH, C1′), 98.7 (CH, C8), 77.0 (C_q, C9a), 68.6 (CH, C2), 65.1 (2′-OCH_2), 64.7 (9-OCH_2), 53.4 (C_q, C3), 50.9 (CH, C3a), 41.1 (NCH_2), 21.8 (CH_2, C4), 20.9 (CH_2, C5), 19.2 (CH_2, C6), 16.2 (NCH_2CH_3), 14.9 and 14.8 (2′-OCH_2CH_3 and 9-OCH_2CH_3), 13.7 (2-CH_3). − IR (diffuse reflection): $\tilde{\nu}$ = 2965.2, 1694.0, 1649.4, 1596.9 cm^{-1}. − MS (70 eV): *m*/*z* (%): 469 (20) [M^+], 352 (100).

(3*E*)-1,1,1,1,1-Pentacarbonyl-4-[(2-dipropylaminocyclohex-2-enyl)]-2-ethyloxy-4-phenyl-1-tungsta-1,3-butadiene (10c), (3-Ethyloxy-1-phenyl-4,5,6,7-tetrahydroinden-3a-yl)dipropylamine (12c), Dipropyl[2,6-bis(1,1,1,1,1-pentacarbonyl-2-ethyloxy-4-phenyl-1-tungsta-1,3-butadien-4-yl)cyclohex-1-enyl]amine (14c), and 9-Ethyloxy-3-(2-ethyloxyethenyl)-2-ethyl-3,7-diphenyl-1-propyl-2,3,3a,4,5,6-hexahydro-1*H*-1-azacyclopenta[*d*]indene (16c): Pentacarbonyl(1-ethyloxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1**) (121 mg, 0.25 mmol) in 1 mL of $CDCl_3$ was added to (cyclohex-1-enyl)dipropylamine (**7c**)[20] (45 mg, 0.25 mmol) in an NMR tube at 0°C to give an orange solution of compound (3*E*)-**10c**. NMR spectra of this solution were recorded immediately at −30°C. A solution of compound **1** (482 mg, 1.00 mmol) in 3 mL of dichloromethane was added to compound **7c** (153 mg, 0.50 mmol) in a 5-mL screw-top vessel under stirring at 0°C. Chromatography on silica after 14 h at 20°C (column 30 × 2 cm), eluting with *n*-pentane/diethyl ether, 10:1, afforded $W(CO)_6$ and (after a small amount of colored products, which were discarded) a pale-yellow fraction containing compound **12c** [231 mg, 68%, R_f = 0.9 (*n*-pentane/diethyl ether, 10:1, on silica), yellow oil]. When the reaction of the (1-alkynyl)carbene complex **1** with compound **7c** was performed in chloroform instead of dichloromethane, a protonated aminocyclopentadiene **13c** was obtained, from which compound **12c** could be generated by treatment with NaOH/H_2O. Formation of compound **13c** as the sole product required ca. 14 h at 50°C. The counterion of compound **13c** was not identified. To pentacarbonyl(1-ethyloxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1**) (241 mg, 0.50 mmol) in a 5-mL screw-top vessel, a solution of cyclohex-1-enyl-dipropylamine (**7c**) (45 mg, 0.25 mmol) in 4 mL of hexane was added with stirring at 20°C to give a blue to brownish solution. After 14 h at −40°C, black crystals of compound **14c** separated, which were isolated by centrifugation and washed with hexane [103 mg, 36%, R_f = 0.9 (*n*-pentane/

diethyl ether, 10:1, on silica), dec. 80°C]. NMR spectra were recorded at −30°C and showed that the two configurational isomers (3′′*E*,3′*E*)-**14c** and (3′′*E*,3′*Z*)-**14c** were present in a 7:10 ratio. Reaction of compound **1** (241 mg, 0.50 mmol) with compound **7c** (45 mg, 0.25 mmol) in 4 mL of dichloromethane in a 5-mL screw-top vessel for 14 h at 20°C afforded a blue to brownish solution, from which a small amount of compound **14c** was isolated by chromatography on neutral alumina (column 30 × 1 cm) eluting with *n*-pentane/diethyl ether, 10:1, together with a pale-yellow fraction containing *spiro*-tetrahydropyrrole **16c** [93 mg, 75%, R_f = 0.9 (*n*-pentane/diethyl ether, 10:1, on silica), yellow oil].

(3*E*)-10c: ^{1}H NMR ($CDCl_3$, 243 K, 360 MHz): δ = 7.37−7.02 (m, 5 H, Ph), 7.17 (s, 1 H, 3-H), 4.69 (dd, 1 H, ^3J = 3.6 Hz, 6′-H), 4.47 and 4.32 (2 m, 1 H each, diastereotopic OCH_2), 3.25 (m, 1 H, 2′-H), 3.07 and 2.81 (2 m, 2 H each, 2 diastereotopic NCH_2), 2.25, 2.11, and 1.49 (3 m, ratio 1:1:8, 3′-H_2−5′-H_2 and 2 NCH_2CH_2), 0.89 and 0.85 (2 t, 3 H each, 2 $NCH_2CH_2CH_3$), 0.76 (br. t, 3 H, OCH_2CH_3). − ^{13}C NMR ($CDCl_3$, 243 K, 90 MHz): δ = 311.3 (W=C), 204.3 and 197.3 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 147.3 (CH, C3), 146.1, 141.5, and 140.4 (C_q each, C1′, C4, and *i*-C Ph), 128.1, 127.1, and 126.9 (2:2:1, each CH, Ph), 98.7 (CH, C6′), 78.7 (OCH_2), 51.7 (2 NCH_2), 43.2 (CH, C2′), 25.5, 24.2, and 16.7 (each CH_2, C3′−C5′), 20.3 (2 NCH_2CH_2), 13.3 (OCH_2CH_3), 11.6 (2 CH_3, 2 $NCH_2CH_2CH_3$).

12c: ^{1}H NMR ($CDCl_3$, 303 K, 360 MHz): δ = 7.36 and 7.11 (2 m, ratio 4:1 H, Ph), 5.20 (s, 1 H, 2-H), 3.87 (m, 2 H, diastereotopic OCH_2), 2.72, 2.47, 2.19, 1.82, 1.60, 1.31, and 1.19 (7 m, ratio 1:1:1:1:1:4:3 H, diastereotopic 4-H_2−7-H_2 and 2 NCH_2CH_2), 2.65 and 2.33 (2 m, 2 H each, 2 NCH_2), 1.33 (t, 3 H, OCH_2CH_3), 0.82 (t, 6 H, 2 $NCH_2CH_2CH_3$). − ^{13}C NMR ($CDCl_3$, 303 K, 75 MHz): δ = 172.8 (C_q, C3), 137.6 (C_q, *i*-C Ph), 136.3 (C_q, C7a), 131.6 (C_q, C1), 128.3, 128.1, and 127.3 (2:2:1, each CH, Ph), 98.0 (CH, C2), 72.8 (C_q, C3a), 64.8 (OCH_2), 52.0 (2 NCH_2, br.), 35.4 (CH_2, C4), 30.1 (CH_2, C5), 24.1 (CH_2, C7), 22.2 (2 NCH_2CH_2), 20.7 (CH_2, C6), 14.7 (OCH_2CH_3), 12.0 (2 $NCH_2CH_2CH_3$). − IR (diffuse reflection): $\tilde{\nu}$ = 2936.1, 1583.0 cm^{-1}. − MS (70 eV), *m*/*z* (%): 339 (100) [M^+].

14c: (3′′*E*,3′*Z*)-**14c** [(3′′*E*,3′*E*)-**14c**]: ^{1}H NMR (CD_2Cl_2, 243 K, 600 MHz): δ = 7.76 [7.04] (s, 1 H, 3′-H), 7.53 ("d", 2 H, *o*-H 4′-Ph), 7.40−7.01 (m, 8 H, 4′′-Ph and *m*- and *p*-H 4′-Ph), 6.84 [7.02] (s, 1 H, 3′′-H), 5.19 and 5.04 [4.50 and 4.29] (2 m, 1 H each, diastereotopic 2′-OCH_2), 4.50 and 4.29 [4.28 and 4.17] (2 m, 1 H each, diastereotopic 2′′-OCH_2), 3.42 [3.52] (br. m, 1 H, 6-H), 3.06 and 2.89 [2.82 and 2.80] (2 br. m, 1 H each, 2 diastereotopic NCH_2), 2.65, 2.11, 1.67, and 1.65 [2.64, 2.58, 2.38, and 2.24] (4 br. m, 1:1:2:2 H, 3-H_2−5-H_2), 1.82 (t, 3 H, 2′-OCH_2CH_3), 1.25 and 1.10 (2 m, 2 H each, 2 diastereotopic NCH_2CH_2), 0.82 and 0.74 [0.50] (2 m, 6:3 H, 2′′-OCH_2CH_3 and 2 $NCH_2CH_2CH_3$). − ^{13}C NMR (CD_2Cl_2, 243 K, 150 MHz): δ = 313.8 (W=C2′′), 297.3 (W=C2′), 204.7, 204.2, 198.2, and 197.5 [198.5 and 197.4][18] [1:1:4:4, *trans*- and *cis*-CO, 2 $W(CO)_5$], 150.6 (C_q, C4′), 150.2 (C_q, C1), 146.8 [148.2] (CH, C3′′), 146.7 (C_q, C4′′), 144.5 [142.3] (CH, C3′), 143.9 (C_q, *i*-C 4′-Ph), 141.3 (C_q, *i*-C 4′′-Ph), 129.6, 128.9, 128.4, 128.2, 127.9, and 127.6 (1:2:2:2:2:1, each CH, 2 Ph), 125.0 (C_q, C2), 79.9 [77.5] (2′-OCH_2), 79.3 [76.9] (2′′-OCH_2), 53.9 and 41.2 (each NCH_2), 45.4 [46.5] (CH, C6), 32.8, 27.2, and 18.7 [30.7, 25.8, and 21.2] (each CH_2, C3−C5), 22.5 and 20.5 (each NCH_2CH_2), 16.3 [17.4] (2′-OCH_2CH_3), 13.6 [14.1] (2′′-OCH_2CH_3), 11.2 and 11.1 (each $NCH_2CH_2CH_3$). − IR (diffuse reflection): $\tilde{\nu}$ = 2952.8, 2060.6, 1922.6 cm^{-1}. − IR (hexane): $\tilde{\nu}$ (%) = 2063.4 (32), 1940.0 cm^{-1} (100) [ν(C≡O)]. − MS (70 eV): ^{184}W, *m*/*z* (%): 1145 (0) [M^+], 865 (0) [M^+ − 10 CO], 497 (78) [M^+ − 2 $W(CO)_5$], 468 (100). − $C_{44}H_{43}NO_{12}W_2$ (1145.5): calcd. C 46.13, H 3.78, N 1.22; found C 45.78, H 4.07, N 0.89.

16c: ^{1}H NMR ($CDCl_3$, 303 K, 360 MHz): δ = 7.99 (br. m, 2 H, *o*-H 3-Ph), 7.30 and 7.18 (2 m, 4 H each, 7-Ph and *m*-, *p*-H 3-Ph), 6.44 (d, 1 H, ^3J = 13 Hz, 2′-H), 5.20 (s, 1 H, 8-H), 5.15 (d, 1 H, ^3J = 13 Hz, 1′-H), 3.93 (m, 2 H, diastereotopic 9-OCH_2), 3.79 (q, 2 H, 2′-OCH_2), 3.52 (dd, 1 H, 2-H), 3.10 (dd, 1 H, 3a-H), 2.56 and 2.38 (2 m, 1 H each, diastereotopic NCH_2), 2.35 and 2.21 (2 m, 1 H each, diastereotopic 6-H_2), 1.77 and 1.68 (2 m, 1 H each, 2-CH_2), 1.52 (m, 2 H, NCH_2CH_2), 1.40 and 1.32 (2 t, 3 H each, 2′-OCH_2CH_3 and 9-OCH_2CH_3), 1.09 (m, 2 H, 4-H_2), 0.96 (t, 3 H, 2-CH_2CH_3), 0.90 (t, 3 H, $NCH_2CH_2CH_3$), 0.86 and −0.16 (2 m, 1 H each, diastereotopic 5-H_2). − ^{13}C NMR ($CDCl_3$, 303 K, 90 MHz): δ = 172.1 (C_q, C9), 146.1 (CH, C2′), 143.1 (C_q, *i*-C 3-Ph), 137.5 (C_q, *i*-C 7-Ph), 135.3 (C_q, C7), 134.3 (C_q, C6a), 131.6 (CH, *o*-C 3-Ph), 128.1, 127.6, 126.5, 126.3, and 125.8 (2:2:2:1:1, each CH, 7-Ph and *m*-, *p*-C 3-Ph), 113.6 (CH, C1′), 98.7 (CH, C8), 76.8 (C_q, C9a), 76.6 (CH, C2), 65.1 (2′-OCH_2), 64.6 (9-OCH_2), 54.5 (C_q, C3), 50.7 (CH, C3a), 50.1 (NCH_2), 23.9 and 23.0 (2-CH_2 and NCH_2CH_2), 21.9 (CH_2, C4), 20.8 (CH_2, C5), 19.5 (CH_2, C6), 15.5 ($NCH_2CH_2CH_3$), 14.9 (2′-OCH_2CH_3 and 9-OCH_2CH_3), 12.6 (2-CH_2CH_3). − IR (diffuse reflection): $\tilde{\nu}$ = 2959.7, 1647.1, 1596.6 cm^{-1}. − MS (70 eV): *m*/*z* (%): 497 (50) [M^+], 352 (100).

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