"Dimers" and "Trimers" of Tetrahydroindenes and Hexahydroazulenes, Respectively Generated from [2-(1-Cycloalkenyl)ethynyl]carbene Complexes (M = W, Cr) by Cascade Cyclization/Cycloaddition Reactions**

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Abstract: A cascade of cyclization/cycloaddition reactions was triggered by addition of protic oxygen nucleophiles ROH **2** (RO = CH_3CO_2, $PhCO_2$, PhO) to [2-(1-cyclohexenyl)ethynyl]carbene complexes **1b** and **1c** (M = W, Cr, respectively), affording highly strained "dimers" **11/11′** and "trimers" **12** of the carbene ligand. The first reaction step involved the formation of 1-metalla-1,3,5-hexatrienes **7**, which readily gave tetrahydroindenes **8** by π cyclization and extrusion of the metal unit. "Dimers" **11/11′** were generated from tetrahydroindenes **8** by a highly *exo* selective [4+2] cycloaddition of compounds **1b** and **1c** to afford 1-metalla-1,3,5-hexatriene intermediates **9**, and a spontaneous π cyclization of the latter compounds involving the disengagement of the metal unit. Propenylidene cyclohexenes **13/13′** were formed in "ene"-type side reactions to the π cyclization of 1-metalla-1,3,5-hexatrienes **7**, by loss of the metal unit. "Dimers" **11** were transformed into "trimers" **12** by a [4+2] cycloaddition and subsequent π-cyclization of the resulting 1-metalla-1,3,5-hexatriene system. The course of the reaction was elucidated by means of model reactions with (2-phenylethynyl)carbene complex **14**, in which 1-metalla-1,3,5-hexatriene intermediates **16** and **17** were isolated and characterized. Alkynyl benzene derivatives **19** were obtained by an unprecedented ring-expansion of a cyclopentadiene unit of "dimers" **11a** and **11c**, involving the insertion of a carbene carbon atom of compound **14** into a C=C bond. A reaction cascade leading to "dimers" **24/24′** could also be triggered by treatment of compounds **2** with [2-(1-cycloheptenyl)ethynyl]carbene tungsten complex **1d**.

Keywords: alkynes · C−C coupling · carbene complexes · cascade reactions · cyclopentadienyl ligands · tungsten

Introduction

(1-Alkynyl)carbene complexes $[(CO)_5M{=}C(OEt)C{\equiv}CR]$ (M = Cr, W) have been utilized as stochiometric reagents in a number of high-yielding transformations potentially useful in organic synthesis.[2] We previously reported on the formation of cyclopentadiene rings[3] by π cyclization of 1-metalla-1,3,5-hexatrienes,[4] which were generated from [2-(1-cycloalkenyl)ethynyl]carbene complexes **1a–d** by addition of protic nucleophiles NuH (NuH = R_2NH,[5] R_2PH,[5] RC(=O)OH and ROH,[6] RC(=X)SH (X = O, NH, NR),[7] and RSH[1]).[8] Whilst addition of nitrogen, phosphorus, and sulfur nucleophiles resulted in production of cyclopentadiene complexes, oxygen nucleophiles afforded metal-free cyclopentadienes. It was shown, for example, that addition of ROH (R = aryl, aroyl, and acyl) to the [2-(1-cyclopentenyl)ethynyl]carbene tungsten complex **1a** gave highly reactive tetrahydropentalenes **4** through π cyclization of the 1-tungsta-1,3,5-hexatriene intermediates **3** (Scheme 1).[6] Compounds **4** underwent a cascade of reactions, initiated by [2+2] cycloaddition with (1-alkynyl)carbene complex **1a** to give compounds **5**, from which pentacyclic compounds **6** were finally derived. The reaction between the tetrahydropentalenes **4** and (1-alkynyl)carbene complex **1a** was regioselective and highly *exo* stereoselective. [2+2] Cycloadducts **5** were formed, but no [4+2] cycloadducts, apparently because of the inherent ring-strain of the tetrahydropentalene systems **4**. We now report on studies of homologous ring compounds—namely tetrahydroindenes **8** and hexahydroazulenes **21**—generated by addition of protic oxygen nucleophiles ROH **2** to [2-(1-cyclohexenyl)ethynyl]carbene complexes **1b** and **1c** (see Scheme 2) and [2-(1-cycloheptenyl)ethynyl]carbene complex **1d** (see Scheme 6), respectively, which underwent a quite different type of cascade reactions.

Results and Discussion

Cascade reactions of [2-(1-Cyclohexenyl)ethynyl]carbene complexes 1b and 1c: [2-(1-Cyclohexenyl)ethynyl]carbene

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[+] Crystal structure analyses

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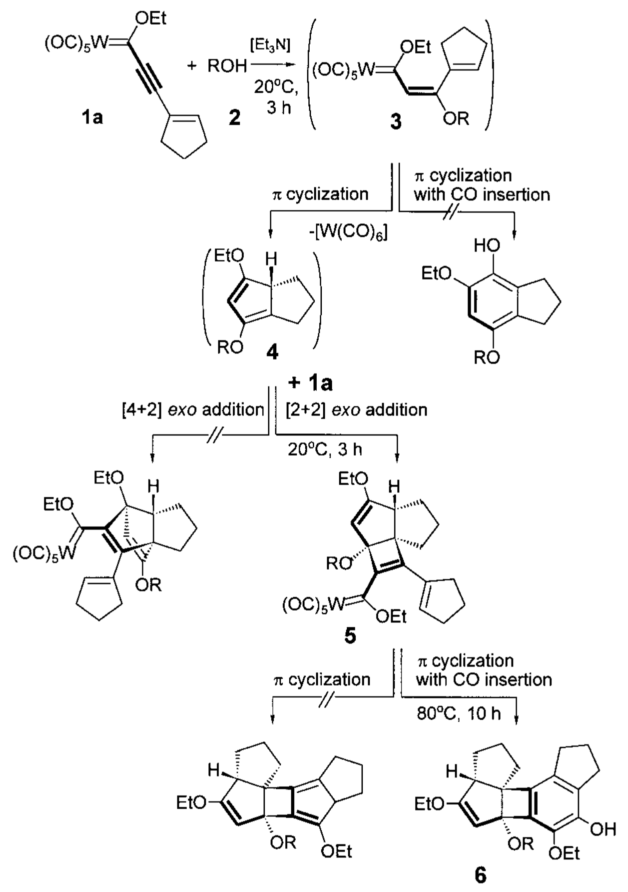
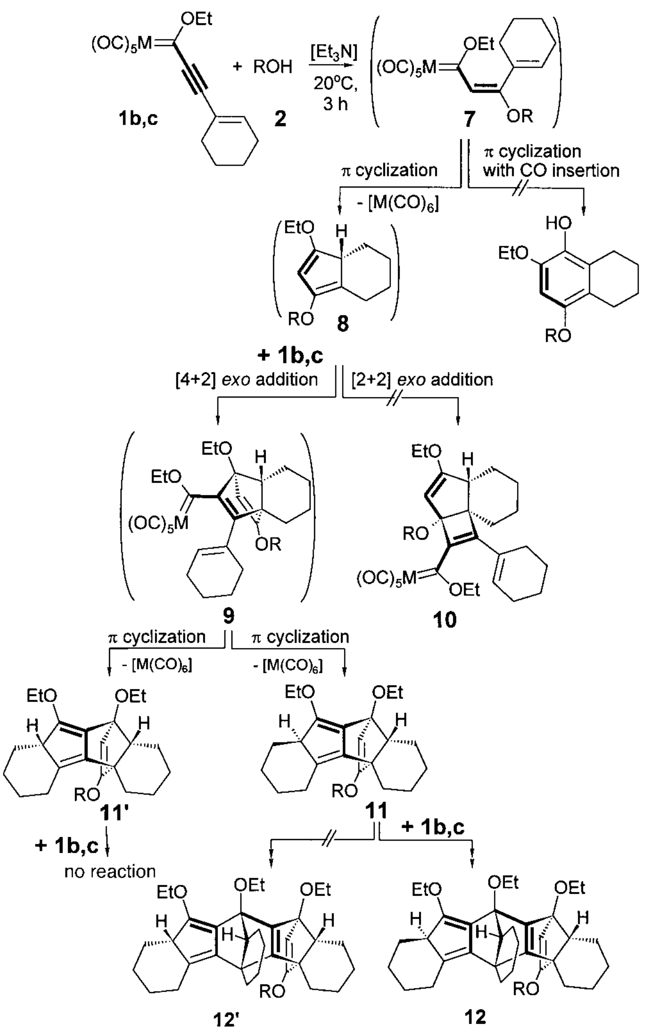


Scheme 1. 1,3-Dioxytetrahydropentalenes **4** from [2-(1-cyclopentenyl)-ethynyl]carbene complex **1a** and [2+2] cycloadducts **5** derived from it.

complexes **1b** and **1c** reacted with protic nucleophiles ROH **2a–c** even at 20°C, if triethylamine was added as catalyst (Scheme 2). Unlike in the corresponding reactions of the [2-(1-cyclopentenyl)ethynyl]carbene complex **1a** (Scheme 1), no stable metal complexes could be isolated in these cases. Only metal-free compounds were obtained: carbene ligand "dimers" **11/11′a–c** and "trimers" **12a–c**, and small amounts of propenylidene cyclohexenes **13/13′a** and **13/13′b**.

The cascade reaction afforded bowl-shaped "oligomers" through a sequence of regioselective and *exo* stereoselective [4+2] cycloaddition reactions of the cyclopentadiene units, generated by π cyclization of 1-metalla-1,3,5-hexatriene precursors, to the C≡C bond of the (1-alkynyl)carbene complexes **1b** and **1c**. Since, for steric reasons, the reactivities of "dimers" **11** towards *exo* [4+2] cycloaddition of compounds **1b** and **1c** are distinctly higher than those of the diastereomers **11′**, the latter compounds accumulated in the reaction mixture. Quite evidently, the stereoinduction of the π cyclization of the 1-metalla-1,3,5-hexatriene unit increases with the progress of oligomerization. Whilst a diastereoselectivity of about 5:3 is achieved for the formation of "dimers" **11/11′**, essentially diastereomerically pure "trimers" **12** are generated from compounds **11** under the influence of the more extended ring system.

The product ratio of compounds **11**:**11′**:**12**:**13**:**13′** depends on the molar ratio of starting components. A shift towards the formation of "trimers" **12** could be experimentally verified if



8–12	M	[a]	RO	(11+11′)[%][b]	12 [%][b]	11:11′:12:13:13′[d]
a	W	1:1	CH_3CO_2	52	15	10:6:3:5:3
a	W	2:1	CH_3CO_2	[c]	[c]	10:3:27:3:1
a	Cr	1:1	CH_3CO_2	63	[c]	10:4:0:0:0
b	W	1:1	$PhCO_2$	25	19	10:4:10:20:6
b	W	2:1	$PhCO_2$	[c]	[c]	10:6:20:10:4
c	W	1:1	PhO	53	21	10:7:5:0:0
c	W	2:1	PhO	[c]	[c]	10:5:15:0:0

[a] Molar ratio of starting components. [b] Yields of isolated products calculated with respect to consumption of (1-alkynyl)carbene complexes **1b** and **1c**, respectively. [c] Yields of isolated products not determined. [d] Molar ratio of products according to ^{1}H NMR spectra of the reaction mixtures. For compounds **13/13′** see Scheme 3.

Scheme 2. "Dimers" **11/11′** and "trimers" **12** from [2-(1-cyclohexenyl)-ethynyl]carbene complexes **1b** and **1c** by a cascade of cyclization/[4+2] cycloaddition reactions. **1b:** M = W; **1c**: M = Cr; **2a**: RO = CH_3CO_2; **2b** $PhCO_2$; **2c**: PhO.

an excess of [2-(1-cyclohexenyl)ethynyl]carbene complex **1b** was applied. The product composition given in Scheme 1 is based on the integration of typical olefinic signals in the ^{1}H NMR spectra of the corresponding reaction mixtures prior to chromatography. A different product ratio was observed after chromatographic work-up, due to the instability of the products (especially of compounds **13/13′**) in solution on contact with silica gel.

Compounds **11** and **11′** could not be separated by chromatography on silica gel, but nevertheless could be fully characterized by NMR spectra, ^{1}J(C,H), ^{2}J(C,H), ^{3}J(C,H) coupling, TOCSY, and NOE experiments, with mixtures displaying two sets of signals. ^{1}H NMR spectra exhibited typical signals for 8-H,[9] 12-H, and 18-H, as well as the diastereotopic protons 9-OCH$_2$ and 11-OCH$_2$ {for example: **11a** [**11′a**]: 8-H, $\delta = 3.04$ [3.13]; 12-H, 2.43 [2.46]; 18-H, 6.51 [6.32]; diastereotopic 9-OCH$_2$, 4.30 and 4.06 [4.23 and 4.07]; diastereotopic 11-OCH$_2$, 3.75 and 3.55 [3.74 and 3.52]}. Further characteristics were supplied by the strong downfield shifts of the bridgehead CH groups C8 and C12 (for example: **11a** [**11′a**]: C8, $\delta = 57.1$ [56.4]; C12, 68.7 [68.5]). The striking lowfield shift of signal C12 was attributed to the bond strain exhibited by the norbornene unit (vide infra). The assignment of the cyclohexyl protons to their appropriate isomers is on the basis of TOCSY experiments.

The coupling patterns of compounds **12** were fully analyzed by NMR spectra, ^{1}J(C,H), ^{2}J(C,H), ^{3}J(C,H) coupling, TOCSY, and NOE experiments. The chemical shifts of signals 8-H,[9] 14-H, 21-H, and 27-H, as well as of the diastereotopic groups 9-OCH$_2$, 11-OCH$_2$, and 13-OCH$_2$ (for example: **12a**: 8-H, $\delta = 2.99$; 14-H, 2.45; 21-H, 2.82; 27-H, 6.55; 9-OCH$_2$, 4.24 and 4.18; 11-OCH$_2$, 3.88 and 3.61; 13-OCH$_2$, 3.81 and 3.45) are found in a typical range. A characteristic lowfield shift of the bridgehead CH signals (vide supra) C8, C14, and C21 was found (for example: **12a**: C8, $\delta = 57.5$; C14, 76.5; C21, 66.5). Assignment of proton signals to the different cyclohexyl units is on the basis of TOCSY experiments. NOE enhancements were observed between 8-H[9] and 4-H$_{ax}$ (NOE++), as well as between 8-H and 7-H$_{eq}$ (NOE+).

The structural assignment of "trimer" **12a** was confirmed by a crystal structure analysis (Figure 1). Clearly, the "bowl shape" geometry of the molecule results from two *exo* [4+2] cycloadditions of the cyclopentadiene units of compounds **8** and **11**, respectively, to the $C{\equiv}C$ bond of the (1-alkynyl)carbene complexes. In line with the striking lowfield shift of the carbon signals of the bridgehead CH groups (vide supra), the bond angles of the corresponding carbon atoms (which are numbered subsequently as indicated in Figure 1) are strongly distorted from the "normal" tetrahedral configuration: C4 (C5-C4-C3 120.6°, C5-C4-C9 113.9°, C3-C4-C9 92.9°), C16 (C15-C16-C11 113.0°, C15-C16-C26 119.0°, C11-C16-C26 95.9°) and C23 (C24-C23-C18 103.6°, C24-C23-C22 118.0°, C18-C23-C22 110.5°).

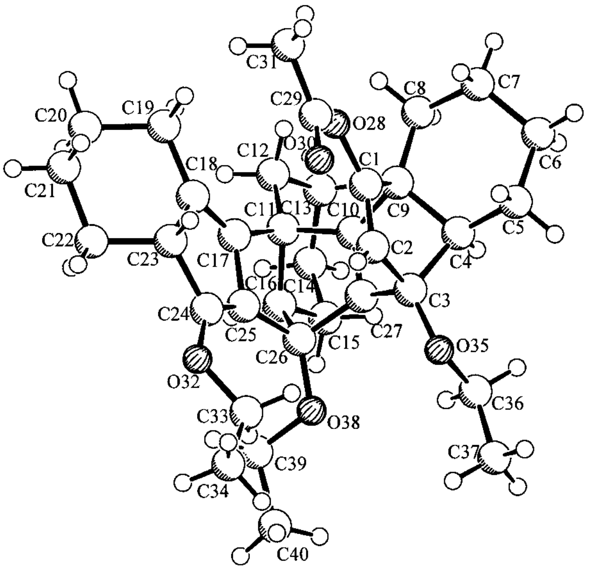
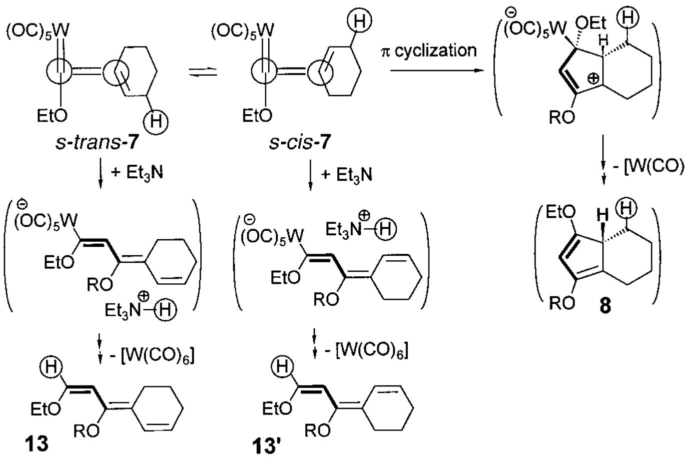


Figure 1. Molecular structure of "trimer" **12a**. Selected bond lengths [Å] and angles [°]: C1–C2 1.314(3), C1–C9 1.543(2), C2–C3 1.542(3), C3–C27 1.528(3), C3–C4 1.561(3), C4–C9 1.562(3), C9–C10 1.525(3), C10–C27 1.337(3), C10–C11 1.535(3), C11–C17 1.524(3), C11–C16 1.552(3), C16–C26 1.567(3), C17–C18 1.333(3), C17–C25 1.478(3), C18–C23 1.517(3), C23–C24 1.511(3), C24–C25 1.345(3), C25–C26 1.540(3), C26–C27 1.510(3); C2-C1-O28 133.8(2), C2-C1-C9 110.6(2), O28-C1-C9 115.6(2), C1-C2-C3 105.3(2), O35-C3-C27 119.4(2), O35-C3-C2 111.2(2), C27-C3-C2 106.7(2), O35-C3-C4 119.9(2), C27-C3-C4 97.0(2), C2-C3-C4 100.1(2), C8-C9-C10 122.7(1), C8-C9-C1 116.2(1), C10-C9-C1 104.9(2), C8-C9-C4 114.2(2), C10-C9-C4 97.2(2), C1-C9-C4 97.3(2), C27-C10-C9 108.0(2), C27-C10-C11 108.9(2), C9-C10-C11 135.8(2), C12-C11-C17 121.9(2), C12-C11-C10 118.0(2), C17-C11-C10 100.6(1), C12-C11-C16 114.9(2), C17-C11-C16 98.8(2), C10-C11-C16 98.5(1), C15-C16-C11 113.0(2), C15-C16-C26 119.0(2), C11-C16-C26 95.9(1), C18-C17-C25 111.9(2), C18-C17-C11 140.6(2), C25-C17-C11 107.0(2), C17-C18-C19 133.7(2), C17-C18-C23 107.3(2), C19-C18-C23 118.9(2), C24-C23-C18 103.6(2), C24-C23-C22 118.0(2), C18-C23-C22 110.5(2), C25-C24-O32 133.8(2), C25-C24-C23 109.7(2), O32-C24-C23 116.5(2), C24-C25-C17 107.5(2), C24-C25-C26 146.8(2), C17-C25-C26 104.8(2), O38-C26-C27 113.9(2), O38-C26-C25 121.3(2), C27-C26-C25 101.7(2), O38-C26-C16 118.3(2), C27-C26-C16 99.4(2), C25-C26-C16 98.6(2), C10-C27-C26 108.7(2), C10-C27-C3 107.3(2), C26-C27-C3 136.2(2).

The marked influence of the ring size of [2-(1-cycloalkenyl)-ethynyl]carbene complexes **1a–c** on the completely different courses of cascade reactions shown in Scheme 1 and Scheme 2 is attributable mainly to two effects: a) the increase in reactivity towards [2+2] cycloadditions to the "bridgehead" C=C bond induced by the higher ring strain in the tetrahydropentalene skeleton **4** relative to the tetrahydroindene skeleton **8**, and b) the large destabilization of the norbornene skeleton resulting from [4+2] cycloaddition of the tetrahydropentalene **4**, due to the ring strain implicit in an annelated cyclopentane ring. Notably the π cyclization of the 1-metalla-1,3,5-hexatriene intermediates is also influenced by ring strain effects. For example, the ring strain induced by the cyclobutene ring annelated to the 1-metalla-1,3,5-hexatriene unit of compounds **5** effects an "atypical" π cyclization involving the insertion of carbon monoxide to give a 1,2-dioxybenzene **6** instead of a cyclopentadiene ring (Scheme 1).[6,8b] Less strained 1-metalla-1,3,5-hexatrienes, like compounds **7** and **9**, undergo a "typical" π-cyclization with formation of a cyclopentadiene ring.[10] "Ene"-type reactions must be taken into account as potential side reactions to the π-cyclization of 1-metalla-1,3,5-hexatrienes which contain hydrogen atoms in allylic positions.[12b] "Ene"-type reactions seem very much to depend on the conformation of α-CH bonds adjacent to the π system under consideration. They are not observed for 1-tungsta-1,3,5-hexatrienes derived from [2-(1-cyclopentenyl)-ethynyl]carbene complexes **1a**, but are observed for 1-tungsta-1,3,5-hexatrienes **7** derived from [2-(1-cyclohexenyl)ethynyl]carbene complexes **1b**. This side reaction affords mixtures of conjugated hexatrienes **13**/**13′**, which are assumed to be derived from the corresponding stereoisomeric 1-tungsta-1,3,5-hexatriene precursors *s-trans*-**7** and *s-cis*-**7**[11] by hydrogen transfer and disengagement of the W(CO)$_5$ unit (Scheme 3).[12] The fact that different amounts of "ene"



13,13′	RO	[13] %[a]	(13/13′)[b]
a	CH_3CO_2	[c]	5:3
b	$PhCO_2$	26	10:3

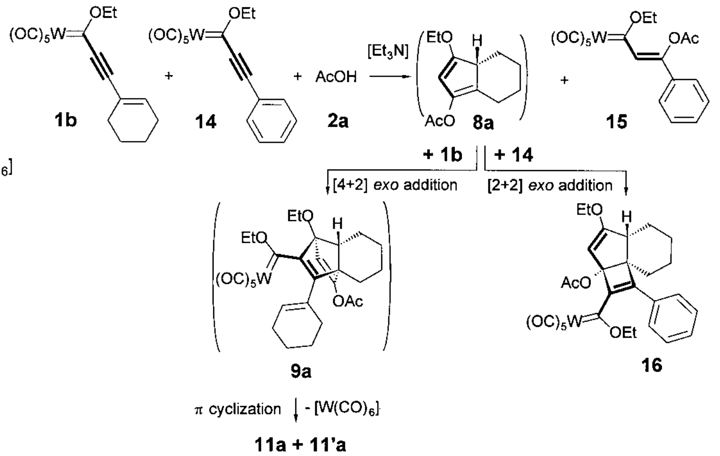
[a] Yields of isolated products in [%] calculated with respect to compound **1b**. [b] Product ratio determined by ^1H NMR spectra. [c] Not isolated.

Scheme 3. Formation of "ene" products **13/13′** in competition with the π cyclization of 1-metalla-1,3,5-hexatrienes.

products are obtained from five- and six-membered ring compounds, respectively, is attributable mainly to ring conformational effects.

The structural assignment for compounds **13/13′** is on the basis of NMR spectra, ^1J(C,H), ^2J(C,H), and ^3J(C,H) coupling, TOCSY, and NOE experiments. The coupling constants of the AB-system of the enol ether unit are in conformity with the *Z* configuration (**13a**: $^3J = 7.2$ Hz; **13′a**: 7.2 Hz). The olefinic protons of the cyclohexene ring show characteristic vicinal couplings (**13a**: $^3J = 9.8$ Hz; **13′a**: 9.8 Hz) and couplings to the neighboring methylene group. An NOE enhancement of the highfield proton 2′-H of the enol ether unit by a ring methylene group 4-H_2 was observed for compound **13a**, but not for its isomer **13′a**.

Trapping of tetrahydroindenes 8 by competition reactions: It has been postulated above that 1,3-dioxy tetrahydroindenes **8** would be generated from [2-(1-cyclohexenyl)ethynyl]carbene complexes **1b** and **1c** via 1-metalla-1,3,5-hexatrienes **7** and would undergo [4+2] cycloadditions with the starting complexes **1b** and **1c** to give 1-metalla-1,3,5-hexatrienes **9** (Scheme 2). We now provide experimental evidence for the intermediacy of tetrahydroindenes **8** by means of competition experiments, in which a mixture of two different (1-alkynyl)-carbene tungsten complexes **1b** and **14** was treated with acetic acid (**2a**)(Scheme 4). The reaction afforded a mixture of products, from which "dimers" **11a/11′a** and a 4-acetoxy-1-tungsta-1,3-butadiene (**15**) were isolated, together with a small amount of a (cyclobutenyl)carbene complex (**16**). The last-mentioned compound apparently results from [2+2] cycloaddition of tetrahydroindene **8a** to (1-alkynyl)carbene complex **14**. It should be noted that compounds **10**, products of [2+2] cycloaddition of [2-(1-cyclohexenyl)ethynyl]carbene complex **1b** to tetrahydroindenes **8** (Scheme 2), were not detected in the reaction mixture, although we cannot rule out their having been formed in very minor quantities.



Scheme 4. Trapping of tetrahydroindene **8a** by competition reactions with different (1-alkynyl)carbene tungsten complexes.

Compound **16** exhibits spectroscopic features typical of (4-oxy-cyclobutenyl)carbene tungsten complexes.[6,13,14] Most notably, the ^{13}C NMR shift of the W=C unit, $\delta = 319.2$, is observed in a range characteristic of nonconjugated 1-tungsta-1,3,5-hexatrienes, thus indicating a presumably strong distortion of the W=C unit relative to the C=C unit and only slight π conjugation resulting from it. Structural characteristics of compound **16** were determined by a crystal structure analysis (Figure 2). The W=C18–C1=C2 component is twisted

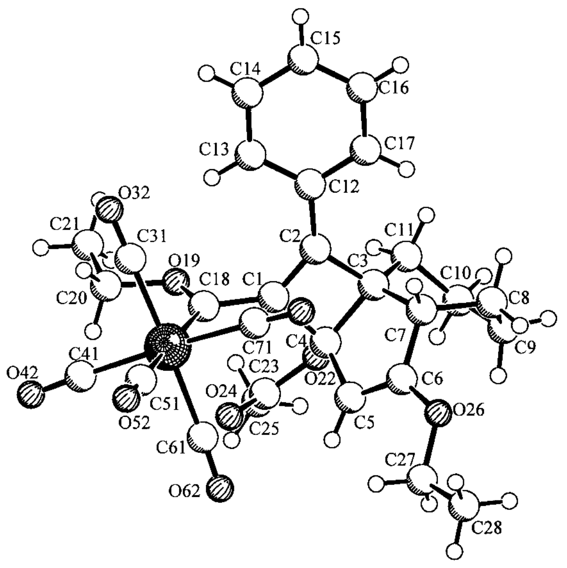
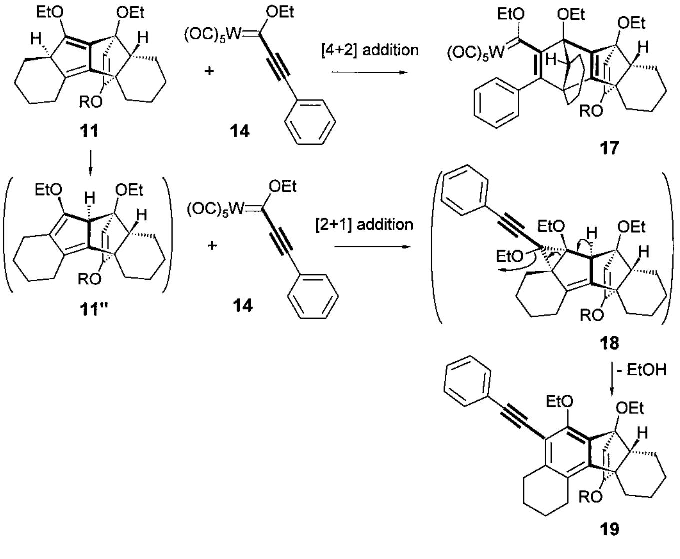


Figure 2. Molecular structure of compound **16**. Selected bond lengths [Å] and angles [°]: C1–C2 1.345(3), C1–C18 1.471(2), C1–C4 1.531(2), C2–C12 1.456(3), C2–C3 1.519(2), C3–C4 1.574(3), C4–O22 1.453(2), C4–C5 1.480(3), C5–C6 1.330(3), C6–C7 1.498(3), C18–O19 1.312(2), C18–W1 2.161(2); C2-C1-C18 135.3(2), C2-C1-C4 93.4(2), C18-C1-C4 131.4(2), C1-C2-C12 134.7(2), C1-C2-C3 95.2(2), C12-C2-C3 130.1(2), C11-C3-C2 116.5(2), C11-C3-C7 112.9(2), C2-C3-C7 116.1(2), C11-C3-C4 117.4(2), C2-C3-C4 85.4(1), C7-C3-C4 105.4(1), O22-C4-C5 114.3(2), O22-C4-C1 112.1(1), C5-C4-C1 121.6(2), O22-C4-C3 113.0(1), C5-C4-C3 106.0(2), C1-C4-C3 86.0(1), C6-C5-C4 109.9(2), C5-C6-O26 129.6(2), C5-C6-C7 115.8(2), O26-C6-C7 114.6(2), C6-C7-C8 113.1(2), C6-C7-C3 102.7(2), C8-C7-C3 113.0(2), O19-C18-C1 106.0(2), O19-C18-W1 133.5(1), C1-C18-W1 120.4(1).

by −91.1(2)°, and the C1=C2–C12=C13 moiety adopts an only slightly tilted *s-trans* arrangement, with an dihedral angle of −12.4(3)°. The cyclohexane ring is forced into a boat conformation by ring strain. The cyclobutenyl ring exhibits a typical trapezoidal shape, characterized by the pattern of bond lengths (C1=C2 1.345(3), C2–C3 1.519(2), C3–C4 1.574(3), C1–C4 1.531(2) Å) and bond angles (C1-C2-C3 95.2(2)°, C2-C3-C4 85.4(1)°, C1-C4-C3 86.0(1)°, C2-C1-C4 93.4(2)°).

[4+2] Cycloaddition and ring-expansion of "dimers" 11: was postulated above that "trimers" **12** would be generated from "dimers" **11** in two steps involving a [4+2] cycloaddition of [2-(1-cyclohexenyl)ethynyl]carbene complex **1b** and a subsequent π cyclization of the adducts. Even though reaction intermediates had not been characterized in this case, we were able to obtain a stable [4+2] cycloadduct **17** from treatment of "dimers" **11a** and **11c** with (2-phenylalkynyl)carbene complex **14** and thus provide evidence of the feasibility of the reaction course postulated above. Compounds **17a** and **17c** were isolated by chromatography in only 22–32% yields, apparently because of their instability on contact with silica gel. The major products of this reaction were compounds **19a** and **19c**, generated by ring-expansion of the cyclopentadiene unit of compounds **11** (Scheme 5). It is assumed that these products are derived from compounds **11″** via fragmentation of cyclopropanation products **18**, although reactions of (1-alkynyl)carbene complexes **1** to give cyclopropanation products have not been reported to date. It may be due to the lower reactivity of (2-phenylalkynyl)carbene complex **14**, relative to [2-(1-cyclohexenyl)ethynyl]carbene complex **1b**, that an appreciable amount of compounds **11** underwent a double bond isomerization to compounds **11″** rather than a [4+2] cycloaddition. Because of the special geometry of the diene portion of compounds **11″**, a [4+2] cycloaddition would afford much more strained adducts than a [2+1] addition ultimately yielding phenylethynyl compounds **19a** and **19c**. Notably, this type of reaction has not been observed on treatment of [2-(1-cyclohexenyl)ethynyl]carbene complex **1b** with "dimers" **11a** and **11c**.

Compounds **17** and **19** were characterized by NMR spectra. The carbon signals of the bridgehead CH groups are observed at very low field (**17a**: $\delta = 71.7$ and 63.7; **17c**: $\delta = 71.7$ and 63.7; **19a**: $\delta = 77.0$; **19c**: $\delta = 76.7$), in a range similar to that observed in compounds **11**, **11′**, and **12** (vide supra). A strong distortion of bond angles at this bridgehead CH moiety was confirmed by the crystal structure analysis of compound **19a** (C22-C21-C28 118.8(3)°, C22-C21-C20 114.0(3)°, and C28-C21-C20 93.3(2)°; Figure 3).



17,19	RO	17 [%][a]	19 [%][a]
a	CH_3CO_2	22	46
c	PhO	32	43

[a] Yields of isolated products.

Scheme 5. [4+2] Cycloaddition and ring-expansion involving the insertion of a carbene carbon atom into a C=C bond of "dimer" **11**.

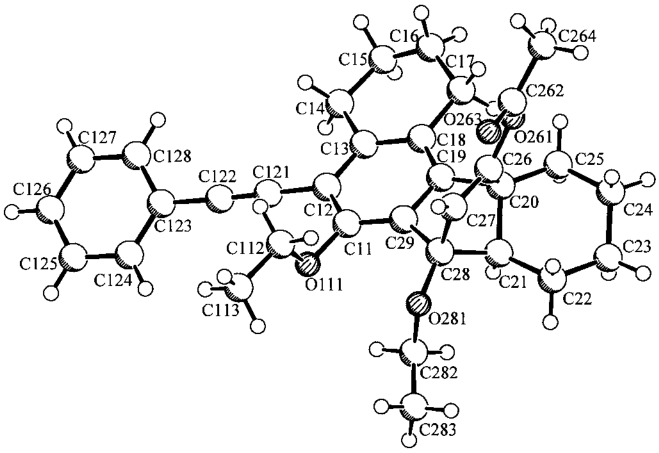
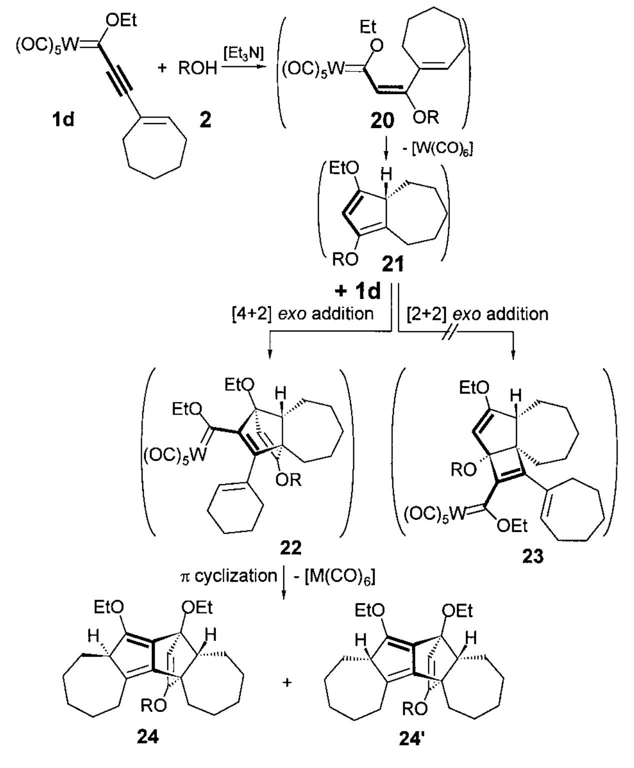


Figure 3. Molecular structure of phenylethynyl compound **19a**. Selected bond lengths [Å] and angles [°]: C11–C29 1.367(5), C11–C12 1.409(4), C12–C13 1.402(4), C12–C121 1.427(5), C121–C122 1.195(5), C122–C123 1.445(5), C13–C18 1.404(5), C18–C19 1.387(4), C19–C29 1.401(4), C19–C20 1.549(4), C20–C21 1.558(4), C20–C26 1.524(4), C21–C28 1.543(5), C26–C27 1.316(4), C26–O261 1.387(4), C27–C28 1.519(5), C28–C29 1.542(4); C29-C11-C12 119.5(3), C13-C12-C11 120.4(3), C13-C12-C121 120.5(3), C11-C12-C121 119.1(3), C122-C121-C12 177.6(4), C121-C122-C123 177.9(4), C12-C13-C18 120.1(3), C12-C13-C14 118.4(3), C18-C13-C14 121.4(3), C19-C18-C13 117.9(3), C19-C18-C17 121.6(3), C13-C18-C17 120.5(3), C18-C19-C29 122.2(3), C18-C19-C20 132.2(3), C29-C19-C20 105.6(3), C25-C20-C26 117.3(3), C25-C20-C19 122.4(3), C26-C20-C19 104.5(3), C25-C20-C21 112.4(3), C26-C20-C21 98.3(2), C19-C20-C21 97.9(2), C22-C21-C28 118.8(3), C22-C21-C20 114.0(3), C28-C21-C20 93.3(2), C27-C26-O261 133.0(3), C27-C26-C20 110.3(3), O261-C26-C20 116.5(3), C26-C27-C28 105.7(3), O281-C28-C27 110.4(3), O281-C28-C21 119.1(3), C27-C28-C21 101.2(3), C27-C28-C29 106.0(3), C21-C28-C29 97.6(2), C11-C29-C19 119.8(3), C11-C29-C28 133.8(3), C19-C29-C28 106.5(3).

Cascade reactions of [2-(1-cycloheptenyl)ethynyl]carbene complex 1d: The strong influence of conformational and ring strain effects on the course of cascade reactions of cyclopentenyl- (**1a**) and (cyclohexenyl)ethynyl carbene complexes (**1b** and **1c**) prompted us to investigate the influence of a seven-membered ring in (2-cycloheptenyl)ethynyl carbene complex **1d**. Compounds **1d** reacted with protic nucleophiles ROH **2a–c** in the presence of triethylamine even at 20°C, to give "dimers" **24/24′** (Scheme 6), as well as propenylidene

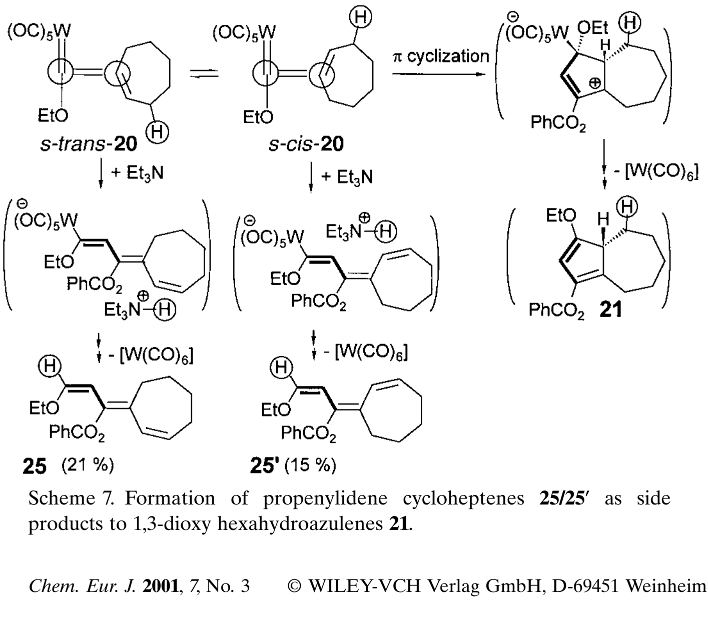


20–24′	[a]	RO	[24 + 24′][b]	24:24′[c]
a	1:1	CH_3CO_2	68	10:4
b	1:1	$PhCO_2$	33	10:4
c	1:1	PhO	59	10:5

[a] Molar ratio of starting components. [b] Yields of isolated products calculated with respect to consumption of (1-alkynyl)carbene complexes **1d**. [c] Molar ratio of products according to ^1H NMR spectra of the reaction mixtures.

Scheme 6. Hexahydroazulenes and "dimers" from (2-cycloheptenyl)-ethynyl carbene complex **1d**.

cycloheptenes **25/25′** (Scheme 7). The results are similar to those observed for the six-membered compounds (Schemes 2 and 3), except that no "trimers" were obtained in this case.



Scheme 7. Formation of propenylidene cycloheptenes **25/25′** as side products to 1,3-dioxy hexahydroazulenes **21**.

Compounds **24/24′** and **25/25′** were fully characterized by NMR spectra. The bridgehead CH groups exhibit lowfield shifts (**24a**: $\delta = 73.1$ and 61.0, **24′a**: $\delta = 73.2$ and 60.0), similar to those observed for the six-membered compounds **11** and **11′** (vide supra). The configuration of compounds **25** and **25′** was assigned in analogy to compounds **13** and **13′**.

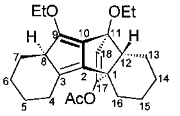
Conclusion

1. "Dimers" **11/11′** and "trimers" **12** were generated from [2-(1-cyclohexenyl)ethynyl]carbene complexes **1b** and **1c** by cascade reactions involving a sequence of highly *exo*-selective [4+2] cycloaddition steps and the π cyclization of 1-metalla-1,3,5-hexatriene intermediates.
2. Propenylidene cyclohexenes were formed by "ene"-type side reactions to the π-cyclization of 1-metalla-1,3,5-hexatrienes.
3. The reaction course of the cascade reactions in Scheme 2 was supported by model reactions with (phenylethynyl) carbene complex **14**, in which metallorganic intermediates could be characterized.
4. A novel ring expansion of a cyclopentadiene **11a** to a benzene derivatives **19** by insertion of a carbene carbon atom into a C=C bond has been found.
5. A strong influence of the ring size of [2-(1-cycloalkenyl)-ethynyl]carbene complexes on the reaction course was observed. Cyclopentadienes attached to cyclohexyl or cycloheptyl rings preferentially undergo [4+2] cycloaddition to (1-alkynyl)carbene complexes **1**, whilst [2+2]- instead of [4+2]-cycloadditions are induced by ring strain in corresponding cyclopentenyl systems.

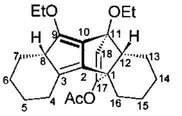
Experimental Section

All operations were carried out under an atmosphere of argon. All solvents were dried and distilled prior to use. All ^1H and ^{13}C NMR spectra were routinely recorded on Bruker ARX 300 and AM 360 instruments. IR spectra were recorded on a Biorad Digilab Division FTS-45 FT-IR spectrophotometer. ^1J(H,C), ^2J (H,C), and ^3J(H,C) decoupling, TOCSY, and NOE experiments were performed on a Bruker AMX 400 instrument if not otherwise indicated. Elemental analyses were determined on a Perkin Elmer 240 elemental analyzer. Analytical TLC plates (Merck DC-Alufolien Kiesegel 60_{F240}), were viewed under UV light (254 nm) and stained using iodine. R_f values refer to TLC tests. Chromatographic purification was performed on Merck Kieselgel 60. Pentacarbonyl(3-cyclohexenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1b**), pentacarbonyl(3-cyclohexenyl-1-ethoxy-2-propyn-1-ylidene)chromium (**1c**), pentacarbonyl(3-cycloheptenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1d**) and pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**14**) were prepared according to the literature.[5]

(*1S*,8R*,11R*,12S)-17-Acetoxy-9,11-diethoxypentacyclo-[9.5.2.0^{1,12}.0^{2,10}.0^{3,8}]octadeca-2,9,17-triene (11a), (*1S*,8S*,11R*,12S**)-17-acetoxy-9,11-diethoxypentacyclo[9.5.2.0^{1,12}.0^{2,10}.0^{3,8}]octadeca-2,9,17-triene (11′a), (*1S*,8R*,11S*,13S*,14R*,19S*,21R**)-26-acetoxy9,11,13-triethoxyoctacyclo[9.9.5.2.0^{1,21}.0^{2,10}.0^{3,8}.0^{12,20}.0^{14,19}]heptacosa-2,9,12,26-tetraene (12a), and 3-(1-acetoxy-3-ethoxypropenylidene)cyclohexene (13a and 13′a):** To pentacarbonyl(3-cyclohex-1-enyl-1-ethoxy-2-propyn-1-ylidene)-tungsten (**1b**, 243 mg, 0.50 mmol) and acetic acid (**2a**, 30 mg, 0.50 mmol) in benzene (1 mL) in a 2 mL air-tight screw-top vessel was added a solution of triethylamine (50 mg, 0.50 mmol) in benzene (1 mL) while stirring. Compound **1b** was completely consumed after about 3 h at 20°C (TLC monitoring). After 8 h at 20°C, a precipitate consisting of $[W(CO)_6]$ was removed by centrifugation and the solvent was replaced by dichloromethane (1 mL). Chromatography on silica gel (column 20 × 2 cm) with *n*-pentane/diethyl ether (20:1) gave a colorless fraction containing compounds **11a** and **11′a** (50 mg, 52 %, **11a**:**11′a** = 3:1, $R_f = 0.8$ in *n*-pentane/diethyl ether (10:1)), a small fraction containing compounds **13a** and **13′a**, as well as a colorless fraction containing compound **12a** (14 mg, 15 %, $R_f = 0.6$ in *n*-pentane/diethyl ether (10:1), colorless crystals from *n*-hexane/diethyl ether (10:1) at −20 °C, m.p. 135 °C). Separation of compounds **11a**, **11′a**, **13a**, and **13′a** on silica gel is possible, but it must be carried out rapidly, since compounds **13a** and **13′a** are quite unstable in solution in contact with silica gel. The product ratio depends on the reaction conditions and is shifted towards the formation of "trimer" **12a** if an excess of compound **1b** is applied. The composition of the product mixtures prior to chromatography was determined by integration of typical olefin signals in the ^{1}H NMR spectra. The reaction between compounds **1b** and **2a** in a molar ratio of 1:1 in benzene at 20 °C gave a product ratio **11a**:**11′a**:**12a**:**13a**:**13′a** of 10:6:3:5:3. Application of a molar ratio of 2:1 gave **11a**:**11′a**:**12a**:**13a**:**13′a** = 10:3:27:3:1. Treatment of acetic acid (**2a**) with pentacarbonyl(3-cyclohex-1-enyl-1-ethoxy-2-propyn-1-ylidene)chromium (**1c**) in a molar ratio of 1:1 in the presence of triethylamine in benzene as described above afforded compounds **11a** and **11′a** (60 mg, 63 %, **11a**:**11′a** = 10:4).

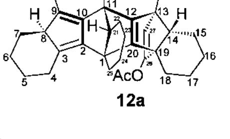


11a



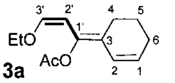
11′a

Compounds 11a [11′a]: ^{1}H NMR (600 MHz, C_6D_6): $\delta = 6.51$ [6.32] (s, 1 H; 18-H), 4.30 and 4.06 [4.23 and 4.07] (1 H each, each m, diastereotopic 9-OCH_2), 3.75 and 3.55 [3.74 and 3.52] (1 H each, each m, diastereotopic 11-OCH_2), 3.04 [3.13] (dd, 1 H; 8-H), 2.43 [2.46] (dd, 1 H; 12-H), 2.63 [2.60] (1 H; 4-H_{eq}), 2.09 [2.05] (1 H; 4-H_{ax}), 2.44 [2.26] (1 H; 7-H_{eq}), 1.28 [1.19] (1 H; 7-H_{ax}); 1.78 and 1.14, 1.61 and 1.10 [1.72 and 1.16, 1.39 and 1.11] (each m, each 1 H; diastereotopic 6-H_2 and 5-H_2); 1.60 and 2.47, 1.57 and 1.92, 1.24 and 1.60, 0.98 and 1.58 [1.61 and 2.39, 1.56 and 1.94, 1.28 and 1.61, 0.95 and 1.60] (each m, each 1 H; diastereotopic 13-H_2–16-H_2), 1.52 [1.58] (s, 3 H; CH_3CO), 1.23 and 1.38 [1.25 and 1.19] (3 H each, each t, each CH_3CH_2O); ^{13}C NMR (C_6D_6): $\delta = 166.9$ [166.7] (C_q, CH_3CO), 154.1 [153.7] (C_q, C17), 151.3 [151.1] (C_q, C9), 143.0 [143.0] (each C_q, C10), 122.4 and 120.9 [122.7 and 120.3] (each C_q, C3 and C2), 115.1 [116.4] (CH, C18), 90.7 [90.6] (C_q, C11), 68.7 [68.5] (CH, C12), 68.1 and 60.7 [68.0 and 60.4] (each CH_2O), 57.1 [56.4] (CH, C8), 52.7 [52.7] (C_q, C1), 31.7 [30.9] (CH_2, C7), 26.0 [26.3] (CH_2, C4), 28.6 and 25.2 [28.7 and 25.3] (each CH_2, C6 and C5); 24.7, 23.9, 23.1, and 22.3 [24.6, 23.9, 23.1, and 22.2] (each CH_2, C13–C16), 20.3 [20.3] (CH_3CO); 15.3 and 15.1 [15.3 and 15.1] (each CH_3CH_2O); IR (hexane): $\tilde{\nu} = 1768$ cm^{-1} (80 %) (ν(C=O)); MS (70 eV): *m/z* (%): 384 (100) $[M]^+$, 325 (96) $[M - CH_3COO]^+$; elemental analysis calcd (%) for $C_{24}H_{32}O_4$ (384.5): C 75.00, H 8.33; found: C 74.89, H 8.24.

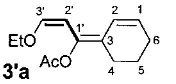


12a

Compounds 12a [12′a]: ^{1}H NMR (600 MHz, C_6D_6): $\delta = 6.55$ (s, 1 H; 27-H), 4.24 and 4.18 (each m, each 1 H, diastereotopic 9-OCH_2), 3.88 and 3.61 (each m, each 1 H, diastereotopic 11-OCH_2), 3.81 and 3.45 (each m, each 1 H, diastereotopic 13-OCH_2), 2.99 (dd, 1 H; 8-H), 2.82 (dd, 1 H; 21-H), 2.45 (dd, 1 H; 14-H), 2.56 (1 H; 4-H_{eq}), 1.74 (1 H; 4-H_{ax}), 2.45 (1 H; 7-H_{eq}), 1,33 (1 H; 7-H_{ax}); 1.73 and 1.20, 1.65, and 1.09 (each m, each 1 H; diastereotopic 6-H_2 and 5-H_2); 2.22 and 1.49, 2.05 and 1.67, 1.62 and 1.08, 1.55 and 1.25 (each m, each 1 H each; diastereotopic 22-H_2–25-H_2); 2.27 and 1.65, 1.95 and 1.56, 1.66 and 1.39, 1.69 and 1.11 (each m, each 1 H, diastereotopic 15-H_2–18-H_2), 1.68 [s, 3 H; CH_3CO]; 1.30, 1.27, and 1.19 (each t, each 3 H, each CH_3CH_2O); ^{13}C NMR (C_6D_6): $\delta = 166.8$ (C_q, CH_3CO), 163.9 and 158.7 (each C_q, C10 and C20), 156.7 (C_q, C9), 156.2 (C_q, C28), 142.5 (C_q, C10), 124.1 and 116.7 (each C_q, C2 and C3), 114.1 (CH, C27), 96.1 (C_q, C13), 93.9 (C_q, C11), 76.5 (CH, C14); 69.1, 62.2, and 61.4 (each OCH_2), 66.5 (CH, C21), 57.5 (CH, C8), 56.8 (C_q, C19), 53.5 (C_q, C1), 31.8 (CH_2, C7), 26.4 (CH_2, C4), 28.8 and 23.9 (each CH_2, C6 and C5); 27.7, 25.2, 22.5, and 22.12 (each CH_2, C15–C18); 25.8, 24.5, 23.3, and 22.6 (each CH_2, C22–C25), 21.0 (CH_3CO); 15.97, 15.80, and 15.54 (each CH_3CH_2O); IR (hexane): $\tilde{\nu} = 1767$ cm^{-1} (80 %) (ν(C=O)); MS (70 eV): *m/z* (%): 546 (69) $[M]^+$, 487 (14) $[M - CH_3COO]^+$; elemental analysis calcd (%) for $C_{35}H_{46}O_5$ (546.7): C 76.89, H 8.48; found: C 76.77, H 8.36. X-ray crystal structure analysis of compound **12a** (code 1208.aum), formula $C_{35}H_{46}O_5$, $M_r = 546.72$ gmol^{-1}, light yellow crystal 0.20 × 0.15 × 0.10 mm, $a = 10.896(2)$, $b = 11.832(2)$, $c = 13.881(3)$ Å, $\alpha = 81.55(2)°$, $\beta = 73.88(2)°$, $\gamma = 64.63(2)°$, $V = 1552.6(5)$ Å^3, $\rho_{calcd} = 1.169$ g cm^{-3}, $\mu = 6.05$ cm^{-1}, empirical absorption correction by ψ scan data ($0.889 \leq T \leq 0.942$), $Z = 2$, triclinic, space group $P\bar{1}$ (no. 2), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 6649 reflections collected ($\pm h$, $+k$, $\pm l$), $[(\sin\phi)/\lambda] = 0.62$ Å^{-1}, 6325 independent ($R_{int} = 0.024$) and 3950 observed reflections [$I \geq 2\sigma(I)$], 365 refined parameters, $R = 0.051$, $wR^2 = 0.131$, max. residual electron density 0.22 (−0.25) e Å^{-3}, hydrogens calculated and refined as riding atoms.[15]



13a



13′a

Compounds 13a [13′a]: ^{1}H NMR (C_6D_6): $\delta = 6.52$ [6.45] (dt, $^3J = 9.8$ [9.8] Hz, $^4J = 2.0$ [2.0] Hz, 1 H; 2-H), 5.77 [5.73] (dt, $^3J = 9.8$ [9.8] Hz and 4.3 [4.4] Hz, 1 H; 1-H), 5.53 [5.60] (d, $^3J = 7.2$ [7.2] Hz, 1 H; 3′-H), 5.06 [5.21] (d, $^3J = 7.2$ [7.2] Hz, 1 H; 2′-H), 3.17 [3.17] (q, 2 H; OCH_2), 2.34 [2.41] (t, 2 H; 4-H), 1.97 [1.94] (m, 2 H; 6-H), 1.95 [1.89] (s, 3 H; CH_3CO), 0.56 [0.56] (t, 3 H; CH_3CH_2O); IR (hexane): $\tilde{\nu} = 1767$ cm^{-1} (90 %) (ν(C=O)).

(*1S*,8R*,11R*,12S)-17-Benzoyloxy-9,11-diethoxypentacyclo-[9.5.2.0^{1,12}.0^{2,10}.0^{3,8}]octadeca-2,9,17-triene (11b), (*1S*,8S*,11R*,12S**)-17-benzoyloxy-9,11-diethoxypentacyclo[9.5.2.0^{1,12}.0^{2,10}.0^{3,8}]octadeca-2,9,17-triene (11′b), (*1S*,8R*,11S*,13S*,14R*,19S*,21R**)-26-benzoyloxy-9,11,13-triethoxyoctacyclo[9.9.5.2.0^{1,21}.0^{2,10}.0^{3,8}.0^{12,20}.0^{14,19}]heptacosa-2,9,12,26-tetraene (12b)** and **3-(1-benzoyloxy-3-ethoxypropenylidene)-cyclohexene (13b and 13′b)**: Pentacarbonyl(3-cyclohex-1-enyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1b**, 243 mg, 0.50 mmol) and benzoic acid (**2b**, 61 mg, 0.50 mmol) were treated in the presence of triethylamine (50 mg, 0.50 mmol) in benzene (2 mL) as described above to give compounds **11b** and **11′b** (28 mg, 25 %, **11b**:**11′b** = 2:1, $R_f = 0.6$ in *n*-pentane/diethyl ether (10:1)), compound **12b** (19 mg, 19 %, $R_f = 0.4$ in *n*-pentane/diethyl ether (10:1), colorless crystals, m.p. 140 °C), compound **13b** (24 mg, 17 %, $R_f = 0.4$ in *n*-pentane/diethyl ether (5:1)) and **13′b** (13 mg, 9 %, $R_f = 0.5$ in *n*-pentane/diethyl ether (5:1)). Treatment of compounds **1b** and **2b** in a molar ratio 1:1 in benzene at 20 °C gave a product ratio **11b**:**11′b**:**12b**:**13b**:**13′b** = 10:4:10:20:6. Application of a molar ratio of 2:1 gave **11b**:**11′b**:**12b**:**13b**:**13′b** = 10:6:20:10:4.

Compounds 11b [11′b]: ^{1}H NMR (600 MHz, C_6D_6):[16] $\delta = 8.05$, 7.02, and 6.97 [8.09, 7.07, and 6.99] (2:1:1 H; Ph), 6.66 [6.50] (s, 1 H; 18-H), 4.19 and 4.07 [4.22 and 4.09] (each m, each 1 H, diastereotopic 9-OCH_2), 3.74 and 3.56 [3.73 and 3.54] (each m, each 1 H, diastereotopic 11-OCH_2), 3.02 [3.12] (dd, 1 H; 8-H), 2.55 [2.58] (dd, 1 H; 12-H), 2.71 [2.67] (m, 1 H; 4-H_{eq}), 2.04 [2.03] (m, 1 H; 4-H_{ax}), 2.46 [2.34] (m, 1 H; 7-H_{eq}), 1.32 [1.31] (m, 1 H; 7-H_{ax}); 1.73 and 1.14, 1.61 and 1.13 [1.73 and 1.17, 1.68 and 1.10] (each m, each 1 H, diastereotopic 6-H_2 and 5-H_2); 2.46 and 1.58, 1.90 and 1.55, 1.59 and 1.22, 1.57 and 0.96 [2.32 and 1.59, 1.92 and 1.56, 1.61 and 1.30, 1.57 and 0.90] (each m, each 1 H, diastereotopic 13-H_2–16-H_2), 1.23 and 1.18 [1.25 and 1.19] (each t, each 3 H, each CH_3CH_2O); ^{13}C NMR (C_6D_6): $\delta = 163.4$ [163.4] (C_q, PhCO), 154.2 [154.4] (C_q, C17), 151.8 [151.8] (C_q, C9); 143.2, 123.0, and 121.2 [143.4, 123.4, and 120.6] (each C_q, C2, C3, and C10); 133.1, 129.9, and 128.6 [133.2, 123.0, and 128.7] (each CH, Ph), 130.4 [130.3] (*i*-C Ph), 116.0 [117.2] (CH, C18), 91.3 [91.2] (C_q, C11), 69.4 [68.9] (CH, C12), 68.5 and 60.4 [68.4 and 60.5] (CH_2O each), 57.6 [56.9] (CH, C8), 53.4 [53.4] (C_q, C1), 31.0 [30.0] (CH_2, C7), 26.3 [26.7] (CH_2, C4), 29.0 and 25.6 [29.2 and 25.6] (CH_2 each, C6 and C5); 25.3, 24.3, 23.4, and 22.7 [25.2, 24.3, 23.4, and 22.6] (each CH_2, C13–C16), 15.6 and 15.5 [15.7 and 15.7] (each CH_3CH_2O); IR (hexane): $\tilde{\nu} = 1745$ cm^{-1} (80 %) (ν(C ∼ O)); MS (70 eV): *m/z* (%): 446 (24) $[M]^+$, 341 (10) $[M - PhCOO]^+$; elemental analysis calcd (%) for $C_{29}H_{34}O_4$ (446.6): C 78.03, H 7.62; found: C 77.95, H 7.55.

Compound 12b: ^{1}H NMR (600 MHz, C_6D_6):[16] $\delta = 8.11$, 7.09, and 7.06 (2:1:2 H; Ph), 6.85 (s, 1 H; 27-H), 4.38 and 4.17 (each 1 H, each m, diastereotopic 9-OCH$_2$), 3.92 and 3.65 (each 1 H, each m, diastereotopic 11-OCH$_2$), 3.84 and 3.57 (each 1 H, each m, diastereotopic 13-OCH$_2$), 3.11 (dd, 1 H; 8-H), 2.88 (dd, 1 H; 21-H), 2.38 (dd, 1 H; 14-H), 2.46 (m, 1 H; 4-H$_{eq}$), 1.46 (m, 1 H; 4-H$_{ax}$), 2.30 (m, 1 H; 7-H$_{eq}$), 1,35 (m, 1 H; 7-H$_{ax}$); 1.25 and 0.85, 1.30, and 1.02 (1 H each, diastereotopic 6-H$_2$ and 5-H$_2$); 2.38 and 1.49, 2.02 and 1.28, 1.64 and 1.08, 1.54 and 1.28 (1 H each, diastereotopic 22-H$_2$–25-H$_2$); 2.24 and 1.64, 1.95 and 1.54, 1.64 and 1.39, 1.69 and 1.09 (1 H each, diastereotopic 15-H$_2$–18-H$_2$); 1.37, 1.30, and 1.22 (3 H each, each t, each C*H*$_3$CH$_2$O); ^{13}C NMR (C$_6$D$_6$): $\delta = 164.2$ (C$_q$, PhCO), 163.2 and 158.8 (each C$_q$, C12, C20), 156.9 (C$_q$, C9), 156.2 (C$_q$, C26); 142.4, 124.7, and 116.7 (each C$_q$, C2, C9, C10); 133.8, 129.7, and 128.7 (each CH, Ph), 130.9 (*i*-C Ph), 114.8 (CH, C27), 96.2 (C$_q$, C11), 94.0 (C$_q$, C13), 76.4 (CH, C14); 69.2, 62.3, and 61.4 (each CH$_2$O), 66.5 (CH, C21), 57.5 (CH, C8), 57.2 (C$_q$, C19), 53.6 (C$_q$, C1), 31.8 (CH$_2$, C7), 27.8 (CH$_2$, C4), 28.6 and 25.3 (each CH$_2$, C6 and C5); 27.1, 26.0, 24.9, and 23.9 (each CH$_2$, C15–C18); 25.6, 24.6, 23.2, and 22.5 (each CH$_2$, C22–C25); 16.0, 15.9, and 15.6 (each *C*H$_3$CH$_2$O); IR (hexane): $\tilde{\nu} = 1744$ cm^{-1} (80 %) (ν(C=O)); MS (70 eV): *m/z* (%): 608 (10) $[M]^+$, 579 (5) $[M - \mathrm{Et}]^+$, 503 (9) $[M - \mathrm{PhCO}]^+$; elemental analysis calcd (%) for $C_{40}H_{48}O_5$ (608.8): C 78.91, H 7.95; found: C 78.22, H 8.03.

Compounds 13b (13′b): ^{1}H NMR (600 MHz, C$_6$H$_6$):[16] $\delta = 8.29$ [8.30] (m, 2 H; *o*-H Ph), 7.19 [7.19] (m, 3 H; *m*- and *p*-H Ph), 6.66 [6.52] (dt, $^3J = 10.1$ [9.8] Hz, $^4J = 2.0$ [2.1] Hz, 1 H; 2-H), 5.73 [5.71] (dt, $^3J = 10.1$ [9.8] and 4.3 [4.4] Hz, 1 H; 1-H), 5.60 [5.66] (d, $^3J = 7.1$ [7.4] Hz, 1 H; 3′-H), 5.18 [5.32] (d, $^3J = 7.1$ [7.4] Hz, 1 H; 2′-H), 3.16 [3.17] (q, 2 H; OCH$_2$), 2.34 [2.41] (t, 2 H; 4-H), 1.89 [1.94] (m, 2 H; 6-H), 1.55 [1.55] (m, 2 H; 5-H), 0.57 [0.59] (t, 3 H; C*H*$_3$CH$_2$O); ^{13}C NMR (C$_6$D$_6$): $\delta = 163.9$ [164.1] (C$_q$, PhCO), 145.9 [145.5] (C$_q$, C3′), 139.1 [140.7] (C$_q$, C1′), 132.5 [132.5] (CH, C1), 128.1 [128.1] (CH, C2), 122.1 [123.2] (C$_q$, C3); 133.4, 130.5, and 128.3 [132.6, 130.5, and 128.4] (each CH, Ph), 130.1 [129.2] (*i*-C Ph), 98.4 [97.7] (CH, C2′), 69.0 [68.9] (OCH$_2$), 25.8 [26.1] (CH$_2$, C4), 25.6 [25.8] (CH$_2$, C6), 22.6 [22.3] (CH$_2$, C5), 14.7 [14.7] (*C*H$_3$CH$_2$O); IR (hexane): $\tilde{\nu} = 1742$ cm^{-1} (60 %) (ν(C=O)).

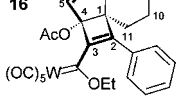
(*1S,*8R**,*11R**,*12S**)-9,11-Diethoxy-17-phenoxypentacyclo-$[9.5.2.0^{1,12}.0^{2,10}.0^{3,8}]$octadeca-2,9,17-triene (11c), (*1S**,*8S**,*11R**,*12S**)-9,11-diethoxy-17-phenoxypentacyclo$[9.5.2.0^{1,12}.0^{2,10}.0^{3,8}]$octadeca-2,9,17-triene (11′c), and (*1S**,*8R**,*11S**,*13S**,*14R**,*19S**,*21R**)-9,11,13-triethoxy-26-phenoxyoctacyclo$[9.9.5.2.0^{1,21}.0^{2,10}.0^{3,8}.0^{12,20}.0^{14,19}]$heptacosa-2,9,12,26-tetraene (12c)**: Pentacarbonyl (3-cyclohex-1-enyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1b**, 243 mg, 0.50 mmol) and phenol (**2c**, 47 mg, 0.50 mmol) were treated in the presence of triethylamine (50 mg, 0.50 mmol) in benzene (2 mL) as described above, over 12 h, to give compounds **11c** and **11′c** (55 mg, 53 %, **11c**:**11′c** = 10:7, $R_f = 0.5$ in *n*-pentane/diethyl ether (10:1)) and compound **12c** (20 mg, 21 %, $R_f = 0.3$ in *n*-pentane/diethyl ether (10:1)). Treatment of compounds **1b** and **2c** in a molar ratio of 1:1 in benzene at 20 °C gave a product ratio of **11c**:**11′c**:**12c** = 10:7:5. Application of a molar ratio of 2:1 gave **11c**:**11′c**:**12c** = 10:5:15.

Compounds 11c [11′c]: ^{1}H NMR (600 MHz, C$_6$D$_6$):[16] $\delta = 7.05$, 6.98, and 6.81 [7.07, 7.02, and 6.82] (2:2:1 H; Ph), 5.05 [5.05] (s, 1 H; 18-H), 4.11 and 3.98 [4.13 and 3.99] (each m, each 1 H, diastereotopic 9-OCH$_2$), 3.65 and 3.43 [3.66 and 3.42] (each m, each 1 H, diastereotopic 11-OCH$_2$), 3.06 [3.11] (dd, 1 H; 8-H), 2.55 [2.61] (dd, 1 H; 12-H), 2.68 [2.64] (m, 1 H; 4-H$_{eq}$), 2.03 [2.03] (m, 1 H; 4-H$_{ax}$), 2.50 [2.39] (m, 1 H; 7-H$_{eq}$), 1.33 [1.23] (m, 1 H; 7-H$_{ax}$); 1.73 and 1.17, 1.66 and 1.18 [1.73 and 1.16, 1.67 and 1.19] (each 1 H, diastereotopic 6-H$_2$ and 5-H$_2$); 2.62 and 1.66, 1.84 and 1.62, 1.63 and 1.18, 161 and 1.13 [2.63 and 1.65, 1.81 and 1.62, 1.62 and 1.01, 1.58 and 1.09] (each 1 H, diastereotopic 13-H$_2$–16-H$_2$), 1.18 and 1.11 [1.17 and 1.10] (each t, each 3 H; each C*H*$_3$CH$_2$O); ^{13}C NMR (C$_6$D$_6$): $\delta = 163.5$ [163.2] (*i*-C PhO), 156.8 [157.6] (C$_q$, C17), 150.7 [150.6] (C$_q$, C9); 143.6, 123.0, and 122.4 [143.7, 123.5, and 121.8] (each C$_q$, C2, C3, and C10); 129.7, 124.3, and 120.4 [129.7, 124.1, and 119.9] (each CH, Ph), 107.3 [105.4] (CH, C18), 90.8 [90.8] (C$_q$, C11), 68.3 [69.3] (CH, C12), 68.1 [68.1] (9-OCH$_2$), 60.9 [60.9] (11-OCH$_2$), 57.5 [56.7] (CH, C8), 53.2 [53.2] (C$_q$, C1), 32.3 [31.9] (CH$_2$, C7), 26.4 [26.6] (each CH$_2$, C4), 29.0 and 25.7 [29.4 and 25.7] (each CH$_2$, C6 and C5); 25.1, 24.5, 23.7, and 23.0 [24.9, 24.4, 23.7, and 22.8] (each CH$_2$, C13–C16), 15.7 and 15.5 [15.7 and 15.5] (each *C*H$_3$CH$_2$O); MS (70 eV): *m/z* (%): 418 (100) $[M]^+$, 389 (64) $[M - \mathrm{Et}]^+$, 325 (84) $[M - \mathrm{PhO}]^+$; HRMS: calcd for $C_{28}H_{34}O_3$: 418.25079; found 418.25187.

Compound 12c: ^{1}H NMR (600 MHz, C$_6$D$_6$):[16] $\delta = 7.16$, 7.08, and 6.86 (2:2:1 H; Ph), 5.15 (s, 1 H; 27-H), 4.17 and 4.03 (each m, each 1 H; diastereotopic 9-OCH$_2$), 3.90 and 3.63 (each m, each 1 H; diastereotopic 11-OCH$_2$), 4.17 and 4.03 (each m, each 1 H; diastereotopic 13-OCH$_2$), 3.03 (dd, 1 H; 8-H), 2.97 (dd, 1 H; 21-H), 2.51 (dd, 1 H; 14-H), 2.68 (m, 1 H; 4-H$_{eq}$), 1.76 (m, 1 H; 4-H$_{ax}$), 2.47(m, 1 H; 7-H$_{eq}$), 1,28 (m, 1 H; 7-H$_{ax}$); 1.72 and 1.15, 1.68 and 1.10 (each m, each 1 H; diastereotopic 6-H$_2$ and 5-H$_2$); 2.16 and 1.69, 2.42 and 1.44, 1.62 and 1.24, 1.58 and 1.18 (each m, each 1 H, diastereotopic 22-H$_2$–25-H); 2.48 and 1.64, 2.41 and 1.55, 1.68 and 1.54, 1.66 and 1.12 (each m, each 1 H; diastereotopic 15-H$_2$–18-H$_2$), 1.27, 1.19, and 1.16 (each t, each 3 H; each C*H*$_3$CH$_2$O); ^{13}C NMR (C$_6$D$_6$): $\delta = 166.6$ (C$_q$, PhO), 163.9 and 159.7 (each C$_q$, C12 and C20), 157.4 (C$_q$, C9), 154.9 (C$_q$, C26); 143.2, 128.3, and 123.7 (each C$_q$, C2, C3, and C10); 129.5, 124.0, and 119.8 (each CH, Ph), 103.0 (CH, C27), 95.7 (C$_q$, C13), 93.8 (C$_q$, C11), 77.7 (CH, C14); 69.0, 62.1, and 61.6 (each OCH$_2$), 68.0 (CH, C21), 58.0 (CH, C8), 56.9 (C$_q$, C19), 53.7 (C$_q$, C1), 32.3 (CH$_2$, C4), 26.3 (CH$_2$, C7), 28.9 and 25.2 (each CH$_2$, C6 and C5); 27.8, 24.6, 24.0, and 23.5 (each CH$_2$, C15–C18); 25.8, 24.5, 23.3, and 22.4 (each CH$_2$, C22–C25); 16.0, 15.6, and 15.5 (each *C*H$_3$CH$_2$O); MS (70 eV): *m/z* (%): 580 (100) $[M]^+$, 551 (95) $[M - \mathrm{Et}]^+$, 535 (55) $[M - \mathrm{EtO}]^+$, 487 (86) $[M - \mathrm{PhO}]^+$; elemental analysis calcd (%) for $C_{39}H_{48}O_4$ (580.8): C 80.57, H 8.26; found: C 80.24, H 8.06.

4-Acetoxy-1,1,1,1,1-pentacarbonyl-2-ethoxy-4-phenyl-1-tungsta-1,3-butadiene (15) and (*1S,*4R**,*7R**)-4-acetoxy-3-(1,1,1,1,1-pentacarbonyl-2-ethoxy-1-tungsta-2-ethenyl)-6-ethoxy-2-phenyl-spiro-tricyclo$[5.4.0^{1,4}.0^{1,7}]$-undeca-2,5-diene (16)**: A mixture of pentacarbonyl(3-cyclohex-1-enyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1b**, 243 mg, 0.50 mmol) and pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**14**, 241 mg, 0.50 mmol) in *n*-pentane (1 mL) was treated with acetic acid (**2a**, 60 mg, 1.00 mmol) and triethylamine (100 mg, 0.80 mmol) in diethyl ether (1 mL) in a 2 mL screw-top vessel for 4 h at 20 °C. Flash column chromatography gave a red fraction containing compounds **11a**, **11′a**, and **16** and a brown fraction containing compound **15**. Compound **16** was isolated by crystallization from diethyl ether/*n*-pentane at −20 °C (61 mg, 35 %, $R_f = 0.8$ in *n*-pentane/diethyl ether (10:1), m.p. 108 °C). Compound **15**, in the brown fraction, was identified by comparison of its spectroscopic data with literature values.[17]

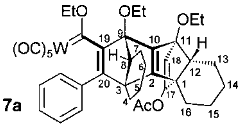
16



Compound 16: ^{1}H NMR (C$_6$D$_6$): $\delta = 7.23$, 7.19, and 7.08 (2:2:1 H; Ph), 5.62 (s, 1 H; 5-H), 4.50 (br, 2 H; diastereotopic W=C-OC*H*$_2$), 3.75 and 3.60 (each m, each 1 H; diastereotopic 6-OCH$_2$), 3.09 (dd, 1 H; 7-H), 2.14 (m, 2 H), 1.91–1.57 (m, 4 H), 1.44 (m, 2 H), 1.75 (s, 3 H; CH$_3$CO), 1.20 and 1.04 (each t, each 3 H, each OCH$_2$C*H*$_3$); ^{13}C NMR (C$_6$D$_6$): $\delta = 319.2$ (br, W=C), 204.3 and 198.0 (each C$_q$, *trans*- and *cis*-CO of W(CO)$_5$), 170.4 (C$_q$, CH$_3$*C*O), 166.1 (C$_q$, C6), 154.4 (C$_q$, C3), 135.9 and 131.8 (each C$_q$, *i*-C Ph and C2); 129.0, 128.9, and 123.0 (each CH, Ph), 96.9 (CH, C5), 91.9 (C$_q$, C4), 79.2 (dynamically broadened W=C-O*C*H$_2$), 65.3 (6-OCH$_2$), 54.0 (C$_q$, C1), 43.2 (CH, C7); 24.9, 23.4, 19.1, and 17.9 (each CH$_2$, C8–C11), 21.0 (*C*H$_3$CO), 14.5 (2 × OCH$_2$*C*H$_3$); IR (hexane) (cm^{-1} (%)): $\tilde{\nu} = 2065.4$ (30), 1940.2 (90), and 1917.1 (100) (ν(C≡O)); 1767 (70) (ν(C=O)); MS (70 eV), *m/z* ^{184}W (%): 704 (20) $[M]^+$, 620 (30) $[M - 3 \times \mathrm{CO}]^+$, 592 (89) $[M - 4 \times \mathrm{CO}]^+$; elemental analysis calcd (%) for $C_{29}H_{28}O_9W$ (704.4): C 49.43, H 3.98; found: C 49.76, H 4.07. X-ray crystal structure analysis of compound **16** (code 1194.aum), formula $C_{29}H_{28}O_9W$, $M_r = 704.36$ gmol^{-1}, orange crystal 0.25 × 0.20 × 0.10 mm, $a = 10.908(1)$, $b = 15.818(1)$, $c = 17.327(1)$ Å, $\beta = 107.59(1)^\circ$, $V = 2849.9(4)$ Å^3, $\rho_{calcd} = 1.642$ g cm^{-3}, $\mu = 41.05$ cm^{-1}, empirical absorption correction by SORTAV ($0.427 \leq T \leq 0.684$), $Z = 4$, monoclinic, space group $P2_1$/n (no. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 11642 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.65$ Å^{-1}, 6507 independent ($R_{int} = 0.017$) and 5876 observed reflections $[I \geq 2\sigma(I)]$, 355 refined parameters, $R = 0.017$, $wR^2 = 0.039$, max. residual electron density 0.45 (−0.88) e Å^{-3}, hydrogens calculated and refined as riding atoms.[15]

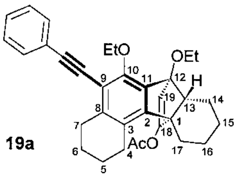
(1*S,3*R**,8*R**,9*R**,11*R**,12*R**)-18-Acetoxy-9,11-diethoxy-19-(1,1,1,1,1-pentacarbonyl-2-ethoxy-1-tungsta-2-ethenyl)-20-phenylhexacyclo-$[9.5.2^{17,18}.2^{19,20}.0^{1,12}.0^{2,10}.0^{3,8}]$eicosa-2,17,19-triene (17a)** and **(1*S**,12*R**,13*R**)-19-Acetoxy-10,12-diethoxy-9-(phenylacetyl)pentacyclo$[10.5.2.0^{1,13}.0^{2,11}.0^{3,8}]$-nonadeca-2,8,10,18-tetraene (19a)**: Pentacarbonyl-(1-ethoxy-3-phenyl-2-propyn-1-ylidene)-tungsten (**14**, 120 mg, 0.25 mmol) was treated with compound **11a** (96 mg, 0.25 mmol) in benzene (2 mL) for 24 h at 20 °C.

Flash column chromatography gave a colorless fraction containing compound **19a** (57 mg, 46%, $R_f = 0.5$ in *n*-pentane/ diethyl ether (10:1), m.p. 208°C) and a red fraction containing compound **17a** (47 mg, 22%, $R_f = 0.4$ in *n*-pentane/diethyl ether (10:1), m.p. 130°C).



17a

Compound 17a: ^1H NMR (C_6D_6): $\delta = 7.37$ (m, 2H; *o*-H Ph), 7.09 (m, 3H; *m*- and *p*-H Ph), 6.26 (s, 1H; 18-H), 4.52 and 4.40 (each m, each 1H; diastereotopic W=C–OCH_2), 4.00 and 3.69 (1H each; diastereotopic 9-OCH_2), 4.00 and 3.60 (each m, each 1H; diastereotopic 11-OCH_2), 2.65 (dd, 1H; 4-H), 2.53 (dd, 1H; 16-H), 2.38 (m, 2H), 1.95 (m; 1H), 1.83–1.50 (m, 7H), 1.66 (s, 3H; CH_3CO), 1.39—1.05 (m, 8H); 1.19, 1.18, and 1.13 (each t, each 3H; each OCH_2CH_3); ^{13}C NMR (C_6D_6): $\delta = 317.0$ (W=C), 203.6 and 197.5 (each C_q, *trans*- and *cis*-CO of $W(CO)_5$), 166.8 (C_q, CH_3CO), 164.0 and 157.5 (each C_q, C17 and C20), 151.7 and 150.6 (each C_q, C2 and C10), 135.9 and 131.7 (each C_q, *i*-C Ph and C19), 128.8, 128.7, and 123.0 (each CH, Ph), 114.8 (CH, C18), 94.5 (C_q, br, C9), 92.8 (C_q, C11), 79.1 (OCH_2), 71.7 (C_q, C12), 65.5 and 60.7 (each OCH_2), 63.7 (CH, C8), 55.3 and 53.8 (each C_q, C1 and C3); 31.0, 27.3, 26.1, 24.4, 24.3, 24.1, 23.3, 22.8, 20.9 (each CH_2, C4—C7 and C13—C16); 16.1, 15.6, and 14.7 (each OCH_2CH_3); IR (hexane): 1767 cm^{-1} (70%) (ν(C=O)); MS (ESI+): *m/z* ^{184}W (%): 867 (20) $[M+H]^+$, 811 (95) $[M-2\times CO]^+$, 783 (40) $[M-3\times CO]^+$, 755 (20) $[M-4\times CO]^+$, 727 (40) $[M-5\times CO]^+$; elemental analysis calcd (%) for $C_{40}H_{42}O_{10}W$ (866.6): C 55.44, H, 4.88; found: C 55.25, H 5.01.



19a

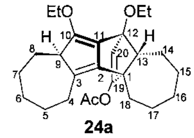
Compound 19a: ^1H NMR (400 MHz, C_6D_6): $\delta = 7.58$ (m, 2H; *o*-H Ph), 7.04 (m, 3H; *m*- and *p*-H Ph), 6.62 (s, 1H; 17-H), 4.25 and 4.08 (each m, each 1H, diastereotopic 10-OCH_2), 3.99 and 3.49 (each m, each 1H; diastereotopic 12-OCH_2), 2.58 (dd, 1H; 13-H), 3.10 and 3.09, 2.81 and 2.81 (each m, each 1H; diastereotopic 4-H_2 and 7-H_2), 1.62 (4H; 5-H_2 and 6-H_2); 2.58 and 1.62, 1.99 and 1.69, 1.72 and 1.23, 1.55 and 1.01 (each m, each 1H, diastereotopic 14-H_2—17-H_2), 1.58 (s, 3H; CH_3CO), 1.49 and 1.39 (each t, each 3H; each OCH_2CH_3); ^{13}C NMR (C_6D_6): $\delta = 166.8$ (C_q, CH_3CO), 161.0 (C_q, C18), 152.5 and 152.1 (each C_q, 2:1, C2, C10, and C11), 140.3 and 138.8 (each C_q, C8 and C9), 116.0 (C_q, C9); 131.8, 128.6, and 127.9 (each CH, Ph), 125.0 (*i*-C Ph), 120.6 (CH, C17), 97.6 and 87.0 (each C_q, C≡C), 92.9 (C_q, C12), 77.0 (CH, C13), 71.0 (10-OCH_2), 61.3 (12-OCH_2), 58.2 (C_q, C1), 29.7 and 27.2 (each CH_2, C4 and C7), 23.5 (2 CH_2, C5 and C6); 26.9, 24.8, 23.3, and 23.1 (each CH_2, C14—C17), 20.5 (CH_3CO), 16.1 and 15.9 (each OCH_2CH_3); IR (hexane): $\tilde{\nu} = 1768$ cm^{-1} (70%) (ν(C=O)); MS (70 eV): *m/z* (%): 496 (70) $[M]^+$, 453 (20) $[M-CH_3CO]^+$, 425 (25) $[M-CH_3COC_2H_5]^+$, 380 (30) $[M-CH_3CO-C_2H_5-C_2H_5O]^+$; elemental analysis calcd (%) for $C_{33}H_{36}O_4$ (496.7): C 79.81, H 7.31; found: C 79.58, H 7.37. X-ray crystal structure analysis of compound **19a** (code 1278.aum), formula $C_{33}H_{36}O_4$, $M_r = 496.62$ $gmol^{-1}$, yellow crystal $0.25\times 0.20\times 0.10$ mm, $a = 10.205(1)$, $b = 16.467(2)$, $c = 16.426(1)$ Å, $\beta = 90.50(1)°$, $V = 2733.2(5)$ Å^3, $\rho_{calcd} = 1.207$ g cm^{-3}, $\mu = 0.78$ cm^{-1}, no absorption correction ($0.981 \leq T \leq 0.992$), $Z = 4$, monoclinic, space group $P2_1/c$ (no. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 7852 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\phi)/\lambda] = 0.59$ Å^{-1}, 4514 independent ($R_{int} = 0.067$) and 2627 observed reflections $[I \geq 2\sigma(I)]$, 338 refined parameters, $R = 0.069$, $wR^2 = 0.158$, max. residual electron density 0.31 (−0.27) e Å^{-3}, hydrogens calculated and refined as riding atoms.[15]

(1*S,3*R**,8*R**,9*R**,11*R**,12*R**)-9,11-Diethoxy-19-(1,1,1,1,1-pentacarbonyl-2-ethoxy-1-tungsta-2-ethenyl)-18-phenoxy-20-phenylhexacyclo-[9.5.2^{17,18}.2^{19,20}.0^{1,12}.0^{2,10}.0^{3,8}]eicosa-2,17,19-triene (17c) and (1*S**,12*R**,13*R**)-10,12-diethoxy-19-phenoxy-9-(phenylacetyl)pentacyclo[10.5.2.0^{1,13}.0^{2,11}.0^{3,8}]-nonadeca-2,8,10,18-tetraene (19c):** Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**14**, 120 mg, 0.25 mmol) was added to a solution of compound **11c** (105 mg, 0.25 mmol) in benzene (2 mL) and kept for 24 h at 20°C. Flash column chromatography gave a colorless fraction containing compound **19c** (57 mg, 43%, $R_f = 0.8$ in *n*-pentane/diethyl ether (10:1)) and a red fraction containing compound **17c** (72 mg, 32%, $R_f = 0.6$ in *n*-pentane/diethyl ether (10:1)).

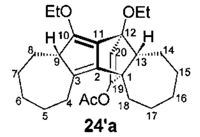
Compound 17c: ^1H NMR (C_6D_6):[16] $\delta = 7.39$ (m, 2H; *o*-H C-Ph), 7.26 (m, 2H; *o*-H OPh), 7.13 (m, 2H; *m*-H O-Ph), 7.06 (m, 3H; *m*- and *p*-H C-Ph), 6.88 (m, 1H; *p*-H O-Ph), 4.96 (s, 1H; 18-H), 4.54 and 4.40 (each m, each 1H; diastereotopic W=C–OCH_2), 3.95 and 3.60, 3.95 and 3.47 (each m, each 1H; diastereotopic 9-OCH_2 and 11-OCH_2), 2.70 (dd; 1H; 8-H), 2.66 (dd; 1H; 12-H), 2.60 (m; 2H), 2.40 (m; 1H), 1.85–1.52 (m; 7H), 1.40–1.05 (m; 8H); 1.15, 1.14, and 1.13 (each t, each 3H; each OCH_2CH_3); ^{13}C NMR (C_6D_6): $\delta = 317.0$ (W=C), 203.8 and 197.6 (each C_q, *trans*- and *cis*-CO of $W(CO)_5$), 163.9 (*i*-C OPh), 160.6 and 157.8 (each C_q, C17 and C20), 155.7 and 150.8 (each C_q, C2 and C10), 136.1 and 131.7 (each C_q, *i*-C C-Ph and C19); 128.8, 128.7, and 123.5 (each CH, C-Ph); 129.9, 124.8, and 120.6 (each CH, O-Ph), 102.0 (CH, C18), 94.2 (C_q, br, C9), 92.6 (C_q, C11), 79.1 (OCH_2), 71.7 (C_q, C12), 65.9 and 60.4 (each OCH_2), 63.7 (CH, C8), 55.4 and 53.8 (each C_q, C1 and C3); 30.7, 30.0, 27.4, 26.3, 24.5, 24.3, 24.2, 23.7, and 23.4 (each CH_2, C5–C8 and C13–C16); 16.1, 15.7, and 14.8 (each OCH_2CH_3); MS (ESI+): *m/z* ^{184}W (%): 901 (20) $[M+H]^+$, 845 (100) $[M-2\times CO]^+$, 817 (40) $[M-3\times CO]^+$, 789 (20) $[M-4\times CO]^+$, 761 (50) $[M-5\times CO]^+$; HSMS: calcd for $C_{44}H_{44}O_9W \sim H$: 902.2611; found 902.1612.

Compound 19c: ^1H NMR (C_6D_6):[16] $\delta = 7.59$ (m, 2H; *o*-H C-Ph), 7.04 (m, 3H; *m*- and *p*-H C-Ph), 6.96 (m, 4H; *o*- and *m*-H O-Ph), 6.81 (1H; *p*-H O-Ph), 5.26 (s, 1H; 19-H), 4.20 and 4.07 (each m, each 1H, diastereotopic 10-OCH_2), 3.97 and 3.49 (each m, each 1H; diastereotopic 12-OCH_2), 2.66 (dd, 1H; 13-H), 3.10 and 3.08, 2.82 and 2,82 (each m, each 1H; diastereotopic 4-H_2 and 7-H_2), 1.61 (4H; 5-H_2 and 6-H_2); 2.57 and 1.60, 2.05 and 1.69, 1.68 and 1.31, 1.55 and 1.10 (each m, each 1H; diastereotopic 14-H_2–17-H_2), 1.39 and 1.37 (each t, each 3H; each OCH_2CH_3); ^{13}C NMR (C_6D_6): $\delta = 169.8$ (*i*-C O-Ph), 157.0 (C_q, C18), 152.5 and 148.7 (2:1, C_q, C2, C10, and C11), 141.2 and 138.8 (each C_q, C8 and C9); 131.8, 129.8, and 127.9 (each CH, C-Ph), 129.2, 124.4, and 120.0 (each CH, O-Ph), 125.2 (*i*-C Ph), 117.0 (C_q, C9), 110.0 (CH, C19), 97.7 and 87.2 (each C_q, C≡C), 93.6 (C_q, C12), 76.7 (CH, C13), 70.8 (10-OCH_2), 61.2 (12-OCH_2), 58.3 (C_q, C1), 29.8 and 27.3 (each CH_2, C4 and C7), 24.0 and 23.7 (each CH_2, C5 and C6), 27.0, 24.5, 23.3, 23.4, and 23.2 (each CH_2, C14–C17), 16.1 and 16.0 (each OCH_2CH_3); MS (ESI+): *m/z* (%): 553 (100) $[M+Na]^+$, 531 (70) $[M+H]^+$; HSMS: calcd for $C_{37}H_{38}O_3+Na$: (553.2719); found 553.2722.

(*1S,*9R**,*12R**,*13S**)-20-Acetoxy-10,12-diethoxypentacyclo-[10.6.2.0^{1,13}.0^{2,11}.0^{3,9}]eicosa-2,10,19-triene (24a) and (*1S**,*9S**,*12R**,*13S**)-20-acetoxy-10,12-diethoxypentacyclo[10.6.2.0^{1,13}.0^{2,11}.0^{3,9}]eicosa-2,10,19-triene (24′a)**: Pentacarbonyl(3-cyclohept-1-enyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1d**, 250 mg, 0.50 mmol), acetic acid (**2a**, 30 mg, 0.50 mmol) in benzene (1 mL), and triethylamine (50 mg, 0.50 mmol) in benzene (1 mL) in a 2 mL screw-top vessel were treated as described above, for 12 h at 20°C, to give compounds **24a** and **24′a** (70 mg, 68%, **24a**:**24′a** = 1:0.4, $R_f =$ 0.6 in *n*-pentane/diethyl ether (10:1)).



24a

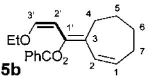


24′a

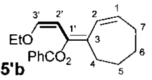
Compounds 24a [24′a]: ^1H NMR (600 MHz, C_6D_6): $\delta = 6.45$ [6.36] (s, 1H; 20-H), 4.14 and 3.96 [4.21 and 3.96] (each m, each 1H; diastereotopic 10-OCH_2), 3.74 and 3.45 [3.74 and 3.44] (each m, each 1H; diastereotopic 12-OCH_2), 3.37 [3.45] (dd, 1H; 9-H), 2.70 [2.64] (dd, 1H; 13-H); 2.59 [2.48] (m, 2H), 2.31 [2.07] (m, 1H), 1.76 [1.67] (m, 2H), 1.55 [1.55] (m, 2H), 1.42 [1.42] (m, 1H) and 1.29 [1.29] (m, 2H; diastereotopic 4-H_2–8-H_2); 2.26 [2.20] (m, 1H), 2.15 [2.12] (m, 1H), 1.87 [1.85] (m, 2H), 1.66 [1.66] (m, 1H), 1.59 [1.59] (m, 2H), 1.52 [1.52] (m, 1H), 1.47 [1.46] (m, 1H) and 1.28 [1.28] (m, 1H; diastereotopic 14-H_2—18-H_2), 1.54 [1.56] (s, 3H; CH_3CO), 1.18 and 1.20 [1.18 and 1.20] (each t, each 3H; each CH_3CH_2O); ^{13}C NMR (C_6D_6): $\delta =$ 167.3 [167.4] (C_q, CH_3CO), 155.6 [155.5] (C_q, C19), 149.4 [149.3] (C_q, C10), 145.1 [145.5] (each C_q, C11), 126.8 and 121.8 [126.6 and 121.7] (each C_q, C2 and C3), 115.7 [116.4] (CH, C20), 89.9 [89.9] (C_q, C12), 73.1 [73.2] (CH, C13), 68.8 and 60.6 [68.4 and 60.6] (each CH_2O), 61.0 [60.0] (CH, C9), 58.1 [58.3] (C_q, C1); 31.7 [30.9], 30.5 [29.9], 30.1 [29.8], 29.7 [29.4], and 28.3 [27.5] (each CH_2, C4—C8); 28.9 [29.1], 27.6 [27.9], 26.6 [26.8], 23.7 [23.6], and 21.8 [21.8] (each CH_2, C14—C18), 20.5 [20.6] (CH_3CO), 15.5 and 15.4 [15.6 and 15.5] (each CH_3CH_2O); IR (hexane): 1767 cm^{-1} (90%) (ν(C=O)); MS (70 eV): m/z (%): 412 (100) $[M]^+$, 369 (20) $[M - CH_3CO]^+$, 367 (30) $[M - C_2H_5O]^+$, 353 (40) $[M - CH_3COO]^+$, 341 (100) $[M - CH_3CO - C_2H_5 + H]^+$, 325 (70) $[M - CH_3CO - C_2H_5O + H]^+$; HRMS: calcd for $C_{26}H_{36}O_4$: 412.26135; found 412.26344.

***(1S*,8R*,12R*,13S*)*-20-Benzoyloxy-10,12-diethoxypentacyclo-[10.6.2.0^{1,13}.0^{2,11}.0^{3,9}]eicosa-2,10,19-triene (24b), *(1S*,8S*,12R*,13S*)*-20-benzoyloxy-10,12-diethoxypentacyclo [10.6.2.0^{1,13}.0^{2,11}.0^{3,9}]eicosa-2,10,19-triene (24′b), and 3-(1-benzoyloxy-3-ethoxypropenylidene)cycloheptene (25b and 25′b)**: Pentacarbonyl(3-cyclohept-1-enyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1d**, 250 mg, 0.50 mmol) and benzoic acid (**2b**, 61 mg, 0.50 mmol) in benzene (1 mL) were treated as described above with triethylamine (50 mg, 0.50 mmol) in benzene (1 mL) in a 2 mL screw-top for 12 h at 20 °C. Fast chromatography on silica gel with *n*-pentane/diethyl ether (20:1) afforded a fraction containing compounds **24b** and **24′b** (39 mg, 33%, **24b**:**24′b** = 1:0.4, $R_f = 0.6$ in *n*-pentane/diethyl ether (10:1)) and compounds **25b**/**25′b** (16 mg, 21%, $R_f = 0.4$ in *n*-pentane/diethyl ether (5:1)).

Compounds 24b [24′b]: ^1H NMR (C_6D_6):[18] $\delta = 8.05$ [8.11] (m, 2H; *o*-H Ph), 7.06 [7.05] (m, 3H; *m*- and *p*-H Ph), 6.55 [6.48] (s, 1H; 20-H), 4.13 and 4.03 [4.16 and 3.98] (each m, each 1H; diastereotopic 10-OCH_2), 3.77 and 3.50 [3.77 and 3.50] (each m, each 1H; diastereotopic 12-OCH_2), 3.35 [3.27] (1H; dd, 9-H), 2.70 [2.65] (1H; dd, 13-H), 2.47–1.25 [2.47–1.25] (20H; 4-H_2–8-H_2 and 14-H_2–18-H_2), 1.21 and 1.20 [1.21 and 1.20] (3H each, each t, each CH_3CH_2O); ^{13}C NMR (C_6D_6): $\delta = 163.6$ [162.5] (C_q, PhCO), 155.7 [155.6] (C_q, C19), 149.6 [149.6] (C_q, C10), 145.1 [145.4] (C_q each, C11); 133.3, 130.0, and 128.6 [133.3, 129.9, and 128.5] (each CH, Ph), 130.4 [130.3] (*i*-C Ph), 127.0 and 121.8 [126.8 and 122.2] (each C_q, C2 and C3), 116.3 [116.9] (CH, C20), 90.1 [90.0] (C_q, C12), 73.6 [73.4] (CH, C13), 68.8 and 61.1 [68.4 and 60.7] (each CH_2O), 61.0 [59.9] (CH, C9), 58.5 [58.4] (C_q, C1); 31.8 [31.6], 30.7 [30.1], 30.1 [29.8], 29.5 [29.4], 28.3 [27.7], 28.9 [29.1], 27.8 [27.9], 26.6 [26.9], 23.7 [23.6] and 21.9 [21.8] (each CH_2, C4–C8 and C14–C18), 15.6 and 15.4 [15.6 and 15.4] (each CH_3CH_2O); IR (hexane): $\tilde{\nu} = 1742$ cm^{-1} (60%) (ν(C=O)); MS (70 eV): m/z (%): 474 (15) $[M]^+$, 445 (6) $[M - C_2H_5]^+$, 429 (5) $[M - C_2H_5O]^+$, 369 (5) $[M - PhCO]^+$; HRMS: calcd for $C_{31}H_{38}O_4$: 474.27701; found 474.27911.



25b



25′b

Compounds 25b [25′b]: ^1H NMR (C_6D_6): $\delta = 8.23$ [8.30] (m, 2H; *o*-H Ph), 7.19 [7.19] (m, 3H; *m*- and *p*-H, Ph), 6.59 [6.47] (dt, $^3J = 11.1$ [11.5] Hz, $^4J = 2.0$ [1.7] Hz, 1H; 2-H), 5.64 [5.76] (dt, $^3J = 11.0$ and 5.5 [11.5 and 4.6] Hz, 1H; 1-H), 5.65 [5.49] (d, $^3J = 7.0$ [7.1] Hz, 1H; 3′-H), 5.21 [5.30] (d, $^3J = 6.9$ [7.3] Hz, 1H; 2′-H), 3.15 [3.13] (q, 2H; OCH_2), 2.50 [2.54] (t, 2H; 4-H), 2.06 [2.06] (m, 2H; 7-H), 1.67 [1.66] (m, 4H; 5-H and 6-H), 0.56 [0.57] (t, 3H; CH_3CH_2O); ^{13}C NMR (C_6D_6): $\delta = 164.0$ [164.2] (C_q, PhCO), 145.4 [146.1] (C_q, C3′), 142.2 [141.1] (C_q, C1′), 133.0 [133.2] (CH, C1), 127.8 [127.8] (CH, C2), 126.1 [126.5] (C_q, C3); 132.5, 130.5, and 128.4 [132.6, 130.5, and 128.3] (each CH, Ph), 130.9 [129.4] (*i*-C Ph), 98.2 [98.5] (CH, C2′), 69.0 [68.9] (OCH_2), 29.5 [29.5] (CH_2, C4), 28.6 [28.8] (CH_2, C7), 27.1 and 27.0 [27.4 and 27.2] (each CH_2, C5 and C6), 14.7 [14.7] (CH_3CH_2O); IR (hexane): $\tilde{\nu} = 1742$ cm^{-1} (70%) (ν(C=O)).

***(1S*,9R*,12R*,13S*)*-10,12-Diethoxy-20-phenoxypentacyclo-[10.6.2.0^{1,13}.0^{2,11}.0^{3,9}]eicosa-2,10,19-triene (24c) and *(1S*,9S*,12R*,13S*)*-10,12-diethoxy-20-phenoxypentacyclo[10.6.2.0^{1,13}.0^{2,11}.0^{3,9}]eicosa-2,10,19-triene (24′c)**: Pentacarbonyl(3-cyclohept-1-enyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1d**, 250 mg, 0.50 mmol) and phenol (**2c**, 47 mg, 0.50 mmol) were treated as described above, by addition of triethylamine (50 mg, 0.50 mmol) in 1 mL of benzene, in a 2 mL screw-top over 12 h at 20 °C to give compounds **24c** and **24′c** (65 mg, 59%, **24c**:**24′c** = 2:1, $R_f = 0.8$ in *n*-pentane/diethyl ether (10:1)).

Compounds 24c [24′c]: ^1H NMR (C_6D_6):[18] $\delta = 7.05$ [7.05] (m, 4H; *o*- and *m*-H Ph), 6.84 [6.84] (m, 1H; *p*-H Ph), 5.11 [5.11] (s, 1H; 20-H), 4.09 and 3.94 [4.15 and 3.98] (each m, each 1H; diastereotopic 10-OCH_2), 3.70 and 3.45 [3.70 and 3.45] (each m, each 1H; diastereotopic 12-OCH_2), 3.43 [3.43] (dd, 1H; 9-H), 2.74 [2.68] (dd, 1H; 13-H), 2.65–1.28 [2.65–1.28] (20H; 4-H_2–8-H_2 and 14-H_2–18-H_2), 1.16 and 1.17 [1.16 and 1.17] (each t, each 3H; each CH_3CH_2O); ^{13}C NMR (C_6D_6): $\delta = 164.4$ [164.1] (*i*-C OPh), 157.3 [157.1] (C_q, C19), 148.5 [148.5] (C_q, C10), 145.6 [146.2] (each C_q, C11); 129.7, 124.1, and 120.1 [129.2, 124.1, and 119.9] (each CH, Ph), 127.0 and 123.1 [126.9 and 123.5] (each C_q, C2 and C3), 107.3 [106.4] (CH, C20), 89.7 [89.7] (C_q, C12), 73.3 [72.9] (CH, C13), 68.2 and 65.8 [68.5 and 65.8] (each CH_2O), 61.0 [60.5] (CH, C9), 58.2 [59.8] (C_q, C1); 31.9 [31.7], 30.7 [30.2], 30.1 [29.8], 29.6 [29.3], 28.3 [27.8], 29.0 [29.2], 27.6 [27.4], 26.6 [26.7], 23.8 [23.7], and 22.2 [22.0] (each CH_2, C4–C8 and C14–C18), 15.6 and 15.5 [15.6 and 15.5] (each CH_3CH_2O); MS (70 eV): m/z (%): 446 (100) $[M]^+$, 417 (90) $[M - C_2H_5]^+$, 401 (90) $[M - C_2H_5O]^+$; HRMS: calcd for $C_{30}H_{38}O_3$: 446.28210; found 446.28192.

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structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-145109 (**12a**), CCDC-145110 (**16**), and CCDC-145111 (**19a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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