Highly Selective Formation of [4+2] and [4+3] Cycloadducts of Tetrahydroindenes Generated in Situ from a (1-Alkynyl)carbene Tungsten Complex by the Metalla-1,3,5-hexatriene Route**

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Dedicated to Professor Dieter Hoppe on the occasion of his 60th birthday

Abstract: 1-Amino-3-ethoxytetrahydro-3a*H*-indenes **8** can be readily generated together with pentacarbonyl(pyridine)-tungsten in a template induced three-component reaction of [(1-cyclohexenyl)-ethynyl]carbene tungsten complex **1** with secondary amines **2a–d** and pyridine. Even though the compounds **8** are thermally quite unstable and undergo a fast rearrangement to tetrahydro-7a*H*-indenes **7**, they can be trapped by formation of (rather strained) [4+2] cycloadducts **12** with maleimide **11**. If 1-amino-3-ethoxytetrahydro-3a*H*-indenes **8** are generated in the presence of electron-poor alkynes **2a** and **2b**, they undergo a 1,5-shift to give tetrahydro-7a*H*-indenes **7**, which in turn afford [4+2] cycloadducts **4a–d**. Condensation of 1-tungsta-1,3,5-hexatrienes (3*E*)-**5a–d** with 1-metalla-1,3-butadienes **14** (M = Cr, W) give [4+3] cycloadducts **15a–e** of tetrahydro-7a*H*-indenes **7** in good yields with high regio- and stereoselectivity.

Keywords: carbene complexes · chromium · cycloadditions · diene ligands · triene ligands · tungsten

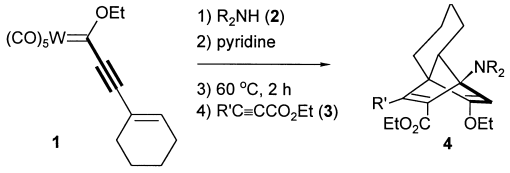
Introduction

(1-Alkynyl)carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CR$ (M = W, Cr; R = aryl, alkenyl) have been applied as stochiometric reagents in a number of high-yielding transformations that have a potential use in organic synthesis.[2] A prominent example is the formation of cyclopentadienes in an overall [3+2] fashion[3] by addition of enamines to (1-alkynyl)carbene complexes; this involves 1-metalla-1,3,5-hexatriene intermediates that rapidly undergo π-cyclization to cyclopentadiene complexes.[4, 5] A different approach to the formation of cyclopentadienes is based on the insertion of alkynes into the Cr=C bond of 1-chroma-1,3-butadienes to initially give 1-chroma-1,3,5-hexatrienes.[6] This approach has been recently extended to include reactions of 1-tungsta-1,3-butadienes, which were found to experience a strong reactivity enhancement under the influence of rhodium or copper catalysts.[1, 7] Furthermore, a most versatile procedure for the anellation of cyclopentadiene rings was found; this involves formation of 1-metalla-1,3,5-hexatrienes from [2-(1-cycloalkenyl)ethynyl]-carbene complexes by addition of protic nucleophiles NuH,[9, 15] for example, R′(RCO)CH_2,[8] R_2NH,[9, 10] R_2PH,[9] RCOOH and ROH,[11, 12] RCXSH (X = O, NH, NR),[13] and RSH.[14]. This last latter approach is suitable for the generation of highly reactive bicyclic cyclopentadienes that can be trapped in situ by cycloaddition[6b, 12] and also by rearrangement reactions.[10, 14]

Results and Discussion

[4+2] Cycloadducts of tetrahydro-3a*H*- and tetrahydro-7a*H*-indenes:We report a simple one-pot procedure, by which tetrahydroindenes are generated from [2-(1-cyclohexenyl)-ethynyl]carbene complex **1** and applied in situ as substrates for [4+2] cycloadditions. An overall reaction leading to tricyclic compounds **4** is outlined in Scheme 1.

It was shown that the addition of one equivalent of a secondary amine **2a–d** to [2-(1-cyclohexenyl)ethynyl]carbene complex **1** at 0 °C affords (3*E*)-4-amino-1-tungsta-1,3,5-



Scheme 1. Highly selective formation of strained tricyclic norbornadiene derivatives **4** by a three-component one-pot reaction of (1-alkynyl)carbene complex **1** (**4a**: R = Me, R′ = Ph; **4b**: R = Me, R′ = H; **4c**: R = pyrrolidino, R′ = Ph).

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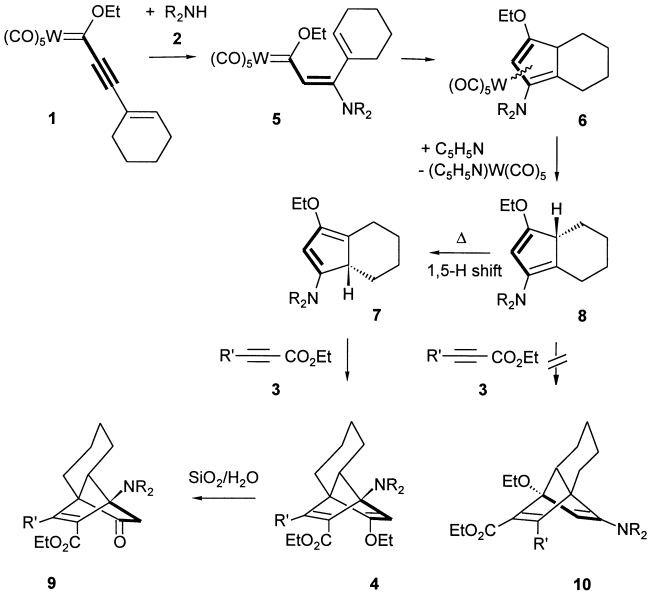
[+] Crystal structure analyses.

[**] Organic Synthesis via Transition Metal Complexes, Part 113. Part 112: see ref. [1].

0947-6539/01/0723-5084 $ 17.50+.50/0

hexatrienes **5a–d**, which were fully characterized. They are stable in the solid state at 0 °C, but in solution they undergo π-cyclization to tetrahydro-3a*H*-indene pentacarbonyltungsten complexes **6**[9] (Scheme 2). The exact coordination site of the pentacarbonyltungsten unit in tetrahydro-3a*H*-indene compounds **6** has not been solved in detail. So far, it can be stated



3	R′	**4**,**9**	R_2N	R′	**4** [%]	**9** [%]
a	Ph	**a**	Me_2N	Ph	75[a]	-
b	H	**b**	Me_2N	H	79[b]	72[a]
		c	pyrrolidino	Ph	78[a]	

5–10	R_2N	**5** [%][c]	**6** [%]	**7**
a	Me_2N	91	87	[e]
b	pyrrolidino	93	[d]	[e]
c	morpholino	90	[d]	[e]
d	(2*S*)-methoxymethyl-pyrrolidino	89	[d]	[e]

[a] Isolated yields after chromatography on silica gel. [b] Yield based on integration of ^{1}H NMR signals of the reaction mixture compared to pentacarbonyl(pyridine)tungsten. [c] Isolated yields after crystallization at −20 °C. [d] Not characterized. [e] Obtained as a 1:1 mixture with pentacarbonyl(pyridine)tungsten according to the integration of the ^{1}H NMR spectrum; characterized by NMR spectra in solution, but not isolated.

Scheme 2. Reaction path to tricyclic [4+2] cycloadducts **4**.

from NMR studies of compound **6a** that the coordination mode is substantially different from that of the corresponding tetrahydropentalene complexes. The latter complexes were shown to exhibit a carbiminium unit and an angular C−W σ bond, in an attempt to relieve the inherent ring strain of the tetrahydropentalene system.[9] Tetrahydro-3a*H*-indenes on the other hand are less strained and seem to favor a (dynamically equilibrating) π coordination. Compounds **6** form yellow oils, which—depending on the 4-amino substituent—may be thermally quite stable. Nevertheless, disengagement of the 1-amino-3-ethoxytetrahydro-3a*H*-indene **8a** from metal complex **6a** was achieved with one equivalent of pyridine at 60 °C. It should be noted that it is the tetrahydro-3a*H*-indenes **8** which are derived from compounds **6** by ligand disengagement with pyridine, even though these compounds are quite unstable and easily undergo a 1,5-H shift to form tetrahydro-7a*H*-indenes **7**.[10] These compounds are quite stable and can be detected in the NMR spectra as the only organic product together with pentacarbonyl(pyridine)tungsten, if compounds **6** (or its precursor **5**) are treated with pyridine at 60 °C for 2 hours.

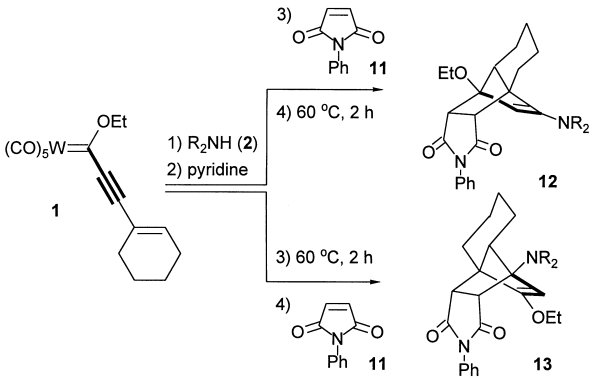
It was anticipated that [4+2] cycloadducts might be derived both from compounds **7** and **8**,[16] depending on the reaction conditions and the nature of the dienophile. The reaction of the 1-tungsta-1,3,5-hexatriene (3*E*)-**5a** with pyridine in presence of PhC≡CCO_2Et (**3a**) at 60 °C for 2 hours was shown to afford a 1:1 mixture of tricyclic compound **4a** and pentacarbonyl(pyridine)tungsten.[17] Since compound **4a** is derived from tetrahydro-7a*H*-indene **7a**, but not from its precursor tetrahydro-3a*H*-indene **8a**, it can be stated that a [4+2] addition of **8a** to electron-poor alkyne **3** to give adduct **10** would be slower than the isomerization of the **8a** to **7a**.[6a, 10] In line with this expectation, compound **4a** was formed as the only product, when a solution of tetrahydro-7a*H*-indene **7a** was prepared first by thermolysis of compound **5a** with pyridine and subsequently treated with the dienophile **3a**. It should be noted that compounds **4** can also be obtained in a three-component one-pot procedure from (1-alkynyl)carbene complex **1** with an astoundingly overall high chemo-, regio-, and stereoselectively. Competing side reactions such as the insertion of alkyne **3** into the M=C bond of a metallahexatriene **5** have not been observed in this case.

Other than outlined above for the [4+2] cycloaddition of electron-poor alkynes **3**, the thermodynamically quite unstable tetrahydro-3a*H*-indenes **8a**,**d** could be captured with the highly reactive olefinic dienophile *N*-phenyl-maleimide (**11**). Reaction of the metallahexatrienes (3*E*)-**5a**,**d** with dienophile **11** in the presence of pyridine at 60 °C for 2 hours gave a 1:1 mixture of pentacarbonyl(pyridine)tungsten and *endo*-[4+2] cycloadducts **12a**,**d**, which are derived from tetrahydro-3a*H*-indenes **8a**,**d** (Schemes 2, 3, and 4).

On the other hand, access to compound **13a** was shown to be provided if tetrahydro-7a*H*-indene **7a** was generated as described above and subsequently treated with dienophile **11** as outlined in Scheme 3. Both the reaction of tetrahydro-3a*H*-indenes **8** and tetrahydro-7a*H*-indenes **7** are highly stereoselective with respect to the formation of *endo*-adducts **12** and **13**, respectively.

The high stereoselectivity of the reactions outlined in Scheme 3 is also exemplified by the fact that a diastereomerically pure[18] [4+2] cycloadduct **12d** was obtained in 81% yield when the (1-alkynyl)carbene complex **1** was treated with (2*S*)-methoxymethylpyrrolidine (**2d**) in the presence of the dienophile **11** (Scheme 4). It is assumed that the reaction involves a highly diastereoselective ring closure by π-cyclization of intermediate **5d** to give a tetrahydro-3a*H*-indene **8d** (Scheme 2). This assumption is in line with previous studies on the ring closure of the corresponding tetrahydropentalene system.[9]

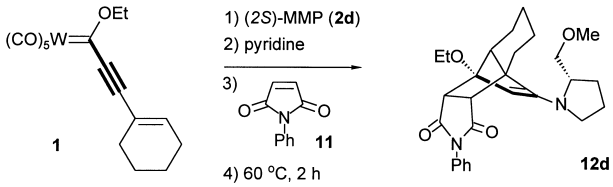
The diastereoselectivity of the [4+2] cycloaddition of tetrahydroindenes was shown to depend strongly on the type



2,12,13	R_2N	12 [%][a]	13 [%][a]
a	Me_2N	85	64
d	(2*S*)-methoxymethylpyrrolidino	81[b]	–

[a] Isolated yield obtained by crystallization. [b] See Scheme 4.

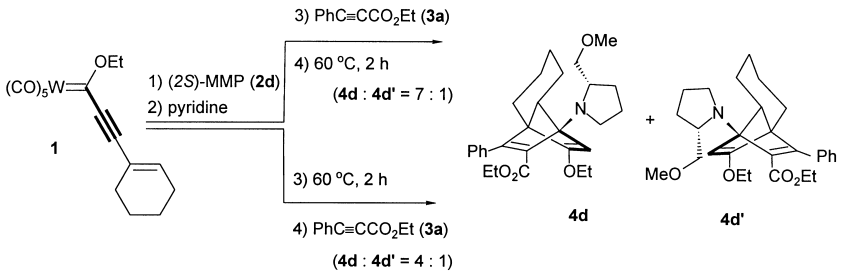
Scheme 3. Selective formation of isomeric tetracyclic norbornene derivatives **12** and **13**, respectively.



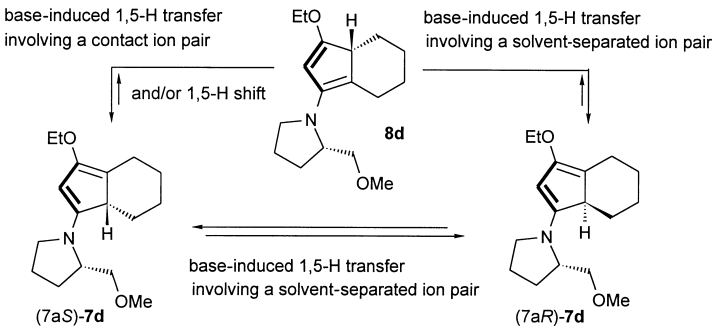
Scheme 4. Formation of a diastereomerically pure [4+2] cycloadduct **12d** induced by (2*S*)-methoxymethylpyrrolidine [(2*S*)-MMP].

of dienophile and also on the reaction conditions. In contrast to the reaction of the 1-tungsta-1,3,5-hexatriene (3*E*)-**5d** with maleimide **11**, which afforded a [4+2] cycloadduct of tetrahydroindene **8d** with high diastereoselectivity (Scheme 4), the reaction of alkyne **3a** was much less selective. It gave a mixture of epimeric [4+2] cycloadducts **4d** and **4d′**, which were derived from the tetrahydroindene isomer **7d** (Schemes 5 and 6). Furthermore, the ratio of compounds **4d** and **4d′** was influenced by the reaction conditions (Scheme 5). Thus, a product ratio of 7:1 was obtained when the tetrahydroindene was generated in the presence of the alkyne **3a**, while a product ratio of 4:1 was observed if the tetrahydroindene was generated first and subsequently treated with the alkyne **3a**.

The lower diastereoselectivity of the [4+2] cycloaddition of the alkyne **3a** compared to maleimide **11** seems to parallel the



Scheme 5. Formation of a 4:1 mixture of epimeric [4+2] cycloadducts **4d** and **4d′** induced by (2*S*)-methoxymethylpyrrolidine [(2*S*)-MMP].



Scheme 6. Interconversion of tetrahydroindenes (3a*R*)-**8d**, (7a*S*)-**7d**, and (7a*R*)-**7d**.

relative reactivity of these dienophiles. It should be noted that the highly reactive olefine dienophile **11** affords a [4+2] cycloadduct of tetrahydroindene **8d**, which is the primary product of the π-cyclization of the 1-metalla-1,3,5-hexatriene **5d**. The less reactive alkyne dienophile **3a** does not give a [4+2] cycloadduct of the tetrahydroindene **8d**, but of its isomers (7a*S*)-**7d** and (7a*R*)-**7d**. These last compounds are assumed to be generated by different processes and also with different rates. It appears that compound (7a*S*)-**7d** would be obtained from the tetrahydroindene **8d** either by a fast 1,5-hydrogen shift and/or by a base-induced fast 1,5-hydrogen transfer that involves a contact ion pair. On the other hand, formation of the epimer (7a*R*)-**7d** is expected to be a somewhat slower process, involving a solvent separated ion pair (Scheme 6). Accordingly, a strong influence of the reaction conditions on the product ratio of compounds **4d** and **4d′** must be encountered. Thermolysis of the 1-tungsta-1,3,5-hexatriene **5d** in the presence of pyridine was found to give an approximate 4:1 mixture of tetrahydroindenes (7a*S*)-**7d** and (7a*R*)-**7d**, according to the NMR spectra. Addition of this mixture to alkyne **3a** afforded a 4:1 ratio of epimers **4d** and **4d′**, which appears to reflect the 4:1 ratio of compounds (7a*S*)-**7d** and (7a*R*)-**7d**. If the thermolysis of 1-tungsta-1,3,5-hexatriene **5d** was performed in the presence of the alkyne **3a**, a 7:1 ratio of epimeric [4+2] cycloadducts was obtained; this indicates that the epimerization of compounds **7d** is somewhat slower than the [4+2] cycloaddition to the alkyne **3a**.

Structure elucidation: Compounds **5** exhibit dynamic NMR spectra resulting from hindered rotation of the (=C)−N-, (=C)−C- and (W=C)−(C=C) single bonds; this has been previously described in more detail for related systems.[9] The molecular structure of compound (3*E*)-**5d** is confirmed by crystal structure analysis (Figure 1). Its W=CC=CC=C backbone exhibits an *all-trans* conformation that includes a slightly elongated "double bond", W−C4 2.261(4) Å, a considerably shortened "single bond", C4−C5 1.397(7) Å, another elongated "double bond", and a short C6−N7 bond 1.328(6) Å ; these indicates a strongly polarized π system, which is best described as a carbiminium carbonylmetalate.

0947-6539/01/0723-5086 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 23

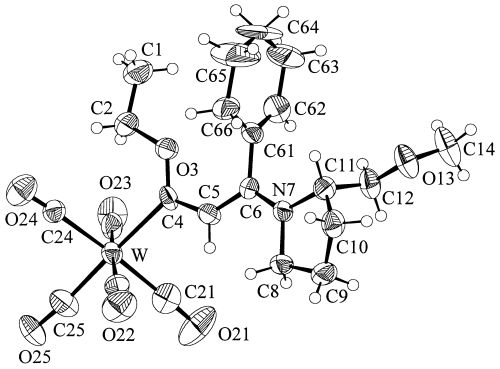


Figure 1. Molecular structure of compound (3*E*)-**5d**. Selected bond lengths [Å] and angles [°]: W–C4 2.261(4), O3–C4 1.345(7), C4–C5 1.397(7), C5–C6 1.404(6), C6–N7 1.328(6), C6–C61 1.512(8), C61–C62 1.304(14); O3-C4-C5 112.8(4), O3-C4-W 128.2(4), C5-C4-W 118.8(4), C4-C5-C6 130.6(5), N7-C6-C5 120.1(4), N7-C6-C61 115.5(5), C5-C6-C61 123.4(5), C62-C61-C66 123.1(7), C62-C61-C6 118.9(10), C66-C61-C6 117.9(10).

Compounds **4**, **12** and **13** were analyzed by COSY, HMQC, and HMBC NMR experiments. A striking feature is the strong down-field shift of the carbon signals of the bridgehead CH units of compounds **4** (e.g., **4a**: C1 $\delta = 60.6$,[19] C6 $\delta = 76.9$; **4b**: C1 $\delta = 58.5$, C6 $\delta = 80.6$; **4c**: C1 $\delta = 61.0$, C6 $\delta = 79.1$), which is attributed to bond distortion within these highly strained systems.[11] A discrimination between isomers **12a** and **13a** is based on the cross-peaks in the two-dimensional HMBC spectrum, which result from the interaction of the protons NCH_3 and OCH_2CH_3 with the carbon skeleton (e.g. $CN(CH_3)_2$ **12a**: $\delta = 80.6$, **13a**: $\delta = 150.3$; $COCH_2$ **12a**: $\delta = 160.2$, **13a**: $\delta = 92.2$), and the characteristic down-field shift of these carbon signals. The stereochemistry of *endo*-adducts **12a** and **13a** was derived from NOE enhancement of the signals 2-H, 6-H, and 12-H on irradiation of 2-H or 6-H.

Compound **4c** was also characterized by crystal structure analysis (Figure 2). In line with the unusual carbon shifts observed in the NMR spectra, the bond angles at the bridgehead carbon atom C1 (C11-C1-C2 120.5(2)°, C11-C1-C7 114.5(2)°, C6-C1-C7 98.5(2)°, C2-C1-C7 98.4(2)°) and C7 (C8-C7-C4 121.6(2)°, C1-C7-C4 92.7(2)°) were found to be strongly distorted. Furthermore, the C1–C11 single bond length of 1.518(3) Å is somewhat shortened.

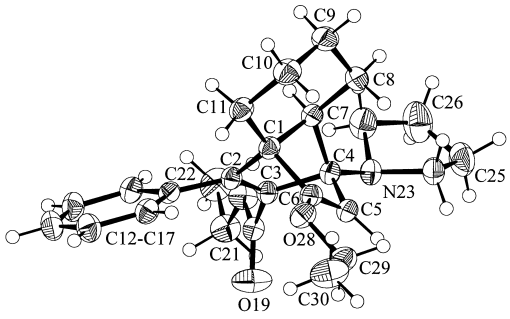
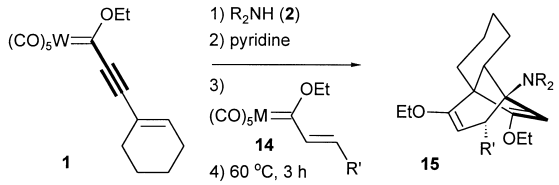


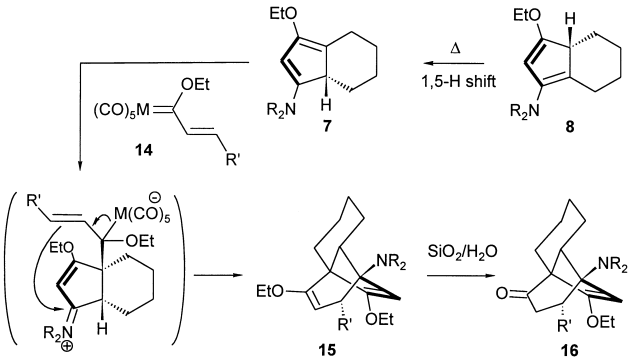
Figure 2. Molecular structure of compound **4c**. Selected bond lengths [Å] and bond angles [°]: C1–C11 1.518(3), C1–C6 1.540(3), C1–C2 1.552(3), C1–C7 1.556(3), C2–C3 1.335(3), C2–C12 1.472(3), C3–C18 1.485(3), C3–C4 1.557(3), C4–N23 1.453(3), C4–C5 1.538(3), C4–C7 1.565(3), C5–C6 1.329(3), C6–O28 1.347(2), C7–C8 1.521(3); C11-C1-C6 116.6(2), C11-C1-C2 120.5(2), C6-C1-C2 104.9(2), C11-C1-C7 114.5(2), C6-C1-C7 98.5(2), C2-C1-C7 98.4(2), C3-C2-C12 128.1(2), C3-C2-C1 106.4(2), C12-C2-C1 125.3(2), C2-C3-C18 127.1(2), C2-C3-C4 108.1(2), C18-C3-C4 124.1(2), N23-C4-C5 116.1(2), N23-C4-C3 113.9(2), C5-C4-C3 105.7(2), N23-C4-C7 121.3(2), C5-C4-C7 100.2(2), C3-C4-C7 96.9(2), C6-C5-C4 105.7(2), C5-C6-O28 133.2(2), C5-C6-C1 109.5(2), O28-C6-C1 117.2(2), C8-C7-C1 113.4(2), C8-C7-C4 121.6(2), C1-C7-C4 92.7(2).

[4+3] Cycloadducts of tetrahydro-3a*H*- and tetrahydro-7a*H*-indenes: 1,3-Dienes have been reported to undergo [4+2] as well as [4+3] cycloadditions to 1-metalla-1,3-butadienes.[20] In our case, the latter reaction was utilized for the generation of strained tricyclic compounds **15** as shown in Scheme 7. It should be noted in this context that compounds **15** are generated by condensation of two different metallaolefines: a 1-metalla-1,3,5-hexatriene and a 1-metalla-1,3-butadiene.



Scheme 7. Highly selective formation of tricyclic compounds **15** from (1-alkynyl)carbene complex **1** and a metalla-1,3-butadiene **14**. (For an explanation of substituents see the table in Scheme 8.)

The scope of the three-component one-pot reactions, as outlined in Schemes 1 and 3 for the formation of classical [4+2] cycloadducts of tetrahydroindene **7** and **8**, could be extended to the formation of [4+3] cycloadducts **15a–e**, which contain unsaturated seven-membered carbocyclic rings. It was shown, for example, that the reaction of the 1-tungsta-1,3,5-hexatriene (3*E*)-**5a** with the 1-tungsta-1,3-butadiene **14a** in the presence of pyridine afforded the tricyco[5.3.2.$0^{1,6}$]dodeca-9,11-diene **15a** in good isolated yields (Scheme 8). It is



14	M	R′	**15**,**16**	NR_2	R′	**15** [%][a]	**16** [%][a,b]
a	W	Ph	**a**	NMe_2	Ph	74	–
b	Cr	Ph	**b**	NMe_2	2-thienyl	71	–
c	W	2-thienyl	**c**	NMe_2	styryl	53	–
d	W	styryl	**d**	morpholino	Ph	56	17
			e	morpholino	2-thienyl	53	16

[a] Isolated yields after chromatography on silica gel. [b] By-product generated by partial hydrolysis of the corresponding enolethers on silica gel.

Scheme 8. Route to [4+3] cycloadducts of tetrahydroindenes **7** by reaction of a 1-metalla-1,3,5-hexatriene with a 1-metalla-1,3-butadiene **14**.

evident that compound **15a** is derived from tetrahydro-7a*H*-indene **7a** by reaction with the 1-tungsta-1,3-butadiene **14a**. The key step of this reaction sequence is assumed to involve a zwitterionic adduct between compounds **7** and the 1-metalla-1,3-butadiene **14a**, which then undergoes a ring-closure induced by a σ,π rearrangement of the $M(CO)_5$ group (Scheme 8). Compounds **15** can be isolated by chromatography on silica gel, allowing that small amounts of ketones **16** are formed by partial hydrolysis.

Compounds **15** and **16** were characterized by COSY, HMQC, and HMBC NMR experiments. The up-field shift of the signals C1 and C6 (e.g., **15a**: C1 $\delta = 51.1$,[19] C6 $\delta = 56.8$; **15b**: C1 $\delta = 51.5$, C6 $\delta = 56.1$; **15d**: C1 $\delta = 51.1$, C6 $\delta = 56.3$) relative to corresponding signals of compounds **4** is attributed to the release of bond strain within the molecules. The regio- and stereochemistry of the [4+3] cycloaddition is deduced from the crystal structure analysis of compound **15d** (Figure 3). The bonds to the bridge-head carbon atom are somewhat distorted, for example, C6-C7-C12 116.5(2)°, C6-C7-C1 105.3(2)°, C12-C7-C1 112.7(2)°, C6-C7-C8 99.0(2)°, C12-C7-C8 114.5(2)°, and slightly shortened, for example, C4–C5 1.517(4), C6–C7 1.515(4) Å.

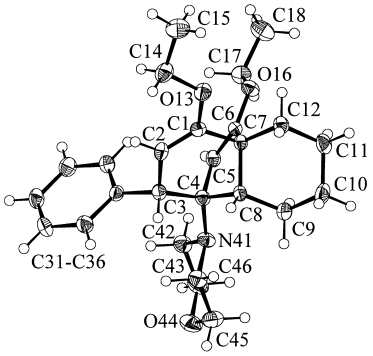
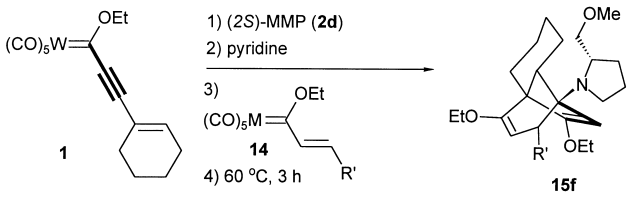


Figure 3. Molecular structure of compound **15d**. Selected bond lengths (Å) and angles (°): C1–C2 1.331(4), C1–C7 1.521(4), C2–C3 1.522(4), C3–C4 1.565(4), C4–C5 1.517(4), C4–C8 1.562(4), C5–C6 1.326(4), C6–C7 1.515(4), C7–C8 1.548(4); C2-C1-C7 121.2(3), C1-C2-C3 122.4(3), C31-C3-C2 111.0(2), C31-C3-C4 117.0(2), C2-C3-C4 114.2(2), N41-C4-C5 111.8(2), N41-C4-C8 111.2(2), C5-C4-C8 100.4(2), N41-C4-C3 114.3(2), C5-C4-C3 113.4(2), C8-C4-C3 104.6(2), C6-C5-C4 109.4(2), C5-C6-O16 131.3(3), C5-C6-C7 111.6(2), O16-C6-C7 116.9(2), C6-C7-C12 116.5(2), C6-C7-C1 105.3(2), C12-C7-C1 112.7(2), C6-C7-C8 99.0(2), C12-C7-C8 114.5(2), C1-C7-C8 107.5(2), C9-C8-C7 112.4(2), C9-C8-C4 114.1(2), C7-C8-C4 100.3(2).

The high selectivity of the [4+3] cycloaddition (Scheme 8) needs some comment, since several different patterns for cycloadditions between 1,3-dienes and 1-metalla-1,3-butadienes have been reported to date. They are influenced by the metal as well as by substituents of the diene system. It has been previously established that 1-metalla-1,3-butadienes (M = Cr, Mo, W) can participate as dienophiles in Diels–Alder reactions.[20a] Formal [2+1] cycloadditions to give vinylcyclopropanes have been also reported and seven-membered rings were obtained by a tandem cyclopropanation/Cope rearrangement.[21] While reactions of 2-amino-1,3-butadienes with 1-tungsta-1,3-butadienes were found to usually afford [4+2] cycloadducts, the corresponding 1-chroma-1,3-butadienes were reported to yield [4+3] cycloadducts.[20c,d] In our reaction, no influence of the metal was observed and both the chromium and the tungsten compound, **14a** and **14b**, respectively, gave the same [4+3] cycloadduct **15a**. So far the reaction behavior of the 1-*tungsta*-1,3-butadiene **14a** to afford a seven-membered carbocyclic ring by [4+3] cycloaddition is unprecedented.[20d, 22] In fact it has been previously reported that the reaction of the 1-tungsta-1,3-butadiene **14a** with enamines would yield cyclopentenes by [3+2] cycloaddition at the carbene carbon atom.[23]

In order to demonstrate the high chemo-, regio-, and stereoselectivity of the template-induced three-component one-pot reaction that lead to compounds **15**, we introduced (*2S*)-methoxymethylpyrrolidine (**2d**) and could isolate diastereomerically pure (according to NMR spectra) compound **15f** in 56% isolated yield (Scheme 9).



Scheme 9. Formation of a diastereomerically pure [4+3] cycloadduct **15f** induced by (*2S*)-methoxymethylpyrrolidine [(*2S*)-MMP].

Conclusion

The thermally induced π cyclization of 4-amino-1-tungsta-1,3,5-hexatrienes (3*E*)-**5a–d**, which are readily available from the [(1-cyclohexenyl)ethynyl]carbene tungsten complex **1** and secondary amines **2a–d**, was shown to provide an efficient access to 1-amino-3-ethoxytetrahydro-3a*H*-indenes **8**. These last compounds are thermally quite unstable, but they can be trapped by formation of [4+2] cycloadducts **12** with very reactive olefinic dienophiles, like the maleimide **11**. Thermolysis of compounds (3*E*)-**5a–d** in the presence of electron-poor alkyne dienophiles **2a**,**b** affords [4+2] cycloadducts **4** of tetrahydro-7a*H*-indene **7**, which result from the isomerization of compounds **8**. Novel [4+3] cycloaddition products **15** have been obtained by addition of 1-metalla-1,3-butadienes **14** (M = Cr, W). The reactions are highly chemo-, regio-, and stereoselective.

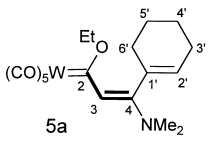
Experimental Section

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 ARX300 and AM360 instruments. COSY, HMQC, HMBC, and NOE experiments were performed on Varian 400 or 600 Hz instruments. IR spectra were recorded on a BIORAD Digilab Division FTS-45 FT-IR spectrophotometer. Elemental analyses were determined on a Perkin–Elmer 240 Elemental Analyzer. Analytical TLC plates, Merck DC-Alufolien Kieselgel 60_{F240}, were viewed by UV light (254 nm) and stained by iodine. R_f values refer to TLC tests. Pentacarbonyl(3-cyclohexenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1**) was prepared according to ref. [9]. 2-Ethoxy-1-pentacarbonylmetalla-1,3-butadienes (M = Cr, W) **14a–d** were prepared according to ref. [24].

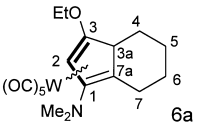
0947-6539/01/0723-5088 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 23

(3*E*)-4-(Cyclohex-1-enyl)-4-(dimethylamino)-2-ethoxy-1-pentacarbonyltungsta-1,3-butadiene [(3*E*)-5a], pentacarbonyl[1-(dimethylamino)-3-ethoxy-4,5,6,7-tetrahydro-3a*H*-indene]tungsten (6a), and 1-(dimethylamino)-3-ethoxy-4,5,6,7-tetrahydro-7a*H*-indene (7a): Dimethylamine (**2a**) (0.50 mmol) in dry diethyl ether (2 mL) was added dropwise to **1** (243 mg, 0.50 mmol) in dry *n*-pentane (1 mL) in a 2 mL screw-top vessel while stirring at 0 °C. The reaction was fast, and the point of equivalency was evident by a color change from brown to yellow. Yellow crystals of compound (3*E*)-**5a** were obtained at −20 °C (241 mg, 91 %, $R_f = 0.7$ in *n*-pentane/dichloromethane 2:1, m.p.: 91 °C). Compound (3*E*)-**5a** (265 mg, 0.50 mmol) in diethyl ether (2 mL) was rearranged completely to give compound **6a** by heating at 35 °C for 24 h (230 mg, 87 %, pale yellow oil). Addition of pentane (2 mL) to the supernatant afforded a further crop of compound **6a**. The rearrangement of (3*E*)-**5a** to **6a** was followed by NMR spectroscopy in $CDCl_3$. Compound **7a** was generated from complex **6a** and pyridine in [D_6]benzene at 60 °C for 2 h together with pentacarbonyl(pyridine)tungsten as indicated by NMR spectra. Compound **7a** was prepared also in a one-pot procedure from compound (3*E*)-**5a** with an equivalent of pyridine in [D_6]benzene at 60 °C for 2 h. Compound **7a** was also obtained in a three-component one-pot procedure starting with compound **1**. Compound **7a** could not be isolated by chromatography on silica gel, but if the reaction mixture was dissolved in *n*-pentane to remove most of pentacarbonyl(pyridine)tungsten by crystallization, **7a** was conveniently accumulated almost pure in solution.

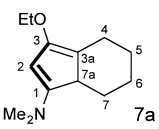
Data for (3*E*)-5a: ^{1}H NMR (300 MHz, C_6D_6, 298 K): $\delta = 6.38$ (s, 1H; 3-H), 5.19 (m, 1H; 2′-H), 4.54 (m, 2H; OCH_2), 2.20 and 2.10 (s, dynamically broadened, 3H each; $N(CH_3)_2$), 1.76 (m, 4H; 3′-H_2, 6′-H_2), 1.39 (m, 4H; 4′-H_2, 5′-H_2), 1.12 (t, 3H; OCH_2CH_3); ^{13}C NMR (C_6D_6): $\delta = 267.7$ (C_q; C2), 204.4 and 200.7 (C_q; *trans*- and *cis*-CO of $W(CO)_5$), 161.1 (C_q; C4), 135.2 (C_q; C1′), 126.8 (CH; C2′), 120.5 (CH; C3), 76.7 (OCH_2), 39.6 (2 CH_3 dynamically broadened; $N(CH_3)_2$), 27.2 and 24.9 (CH_2; C3′, C6′), 22.2 and 21.9 (CH_2; C4′, C5′), 15.8 (OCH_2CH_3); IR (hexane): $\tilde{\nu} = 2058.2$ (5) 1923.2 cm^{-1} (100) (C≡O); MS (70 eV, ^{184}W): *m*/*z* (%): 531 (1) $[M]^+$, 391 (5) $[M-5\,CO]^+$, 207 (100) $[M-W(CO)_5]^+$; elemental analysis calcd (%) for $C_{18}H_{21}NO_6W$ (531.1): C 40.67, H 3.99, N 2.64; found: C 40.60, H 3.43, N 2.83.



Data for 6a: ^{1}H NMR (C_6D_6): $\delta = 4.52$ (s dynamically broadened, 1H; 2-H), 3.64 (m, 2H; diastereotopic OCH_2), 3.58 (dd, $^3J = 6, 6$ Hz, 1H; 3a-H), 3.48 (br s, 6H; NMe_2), 2.2–2.0 and 1.7–1.2 (3:5 H; diastereotopic 4-H_2 to 7-H_2), 1.50 (t, 3H; OCH_2CH_3); ^{13}C NMR (C_6D_6, 233 K): $\delta = 202.6$ and 199.9 (C_q; *trans*- and *cis*-CO of $W(CO)_5$), 194.6 (C_q; C=N), 189.4 (C_q; =COEt), 97.5 (CH; C2), 72.1 (OCH_2), 71.2 (CH; C3a), 45.0 (C_q; C7a), 43.4 and 43.0 ($N(CH_3)_2$), 26.5 (CH_2; C7), 24.0, 22.4 and 21.9 (CH_2; C4–C6), 14.4 (OCH_2CH_3); IR (diffuse reflection): $\tilde{\nu} = 2050.5$ (5), 1943.6 (10), 1891.4 (100) (C≡O) 1584.0 cm^{-1} (20) (NC=C); MS (70 eV, ^{184}W): *m*/*z* (%): 531 (1) $[M]^+$, 391 (5) $[M-5\,CO]^+$, 207 (100) $[M-W(CO)_5]^+$.



Data for 7a: ^{1}H NMR (C_6D_6): $\delta = 5.03$ (s, 1H; 2-H), 3.87 (m, 2H; OCH_2), 2.58 (dd, $^3J = 4.8, 11.7$ Hz, 1H; 7a-H), 2.43 (s, 6H; $N(CH_3)_2$), 3.04 and 2.02 (m, 1:1 H; 4-H_{eq}, 4-H_{ax}), 2.18 and 1.07 (m, 1:1 H; 7-H_{eq}, 7-H_{ax}), 1.76 and 1.18 (m, 1:1 H; 5-H_{eq}, 5-H_{ax}), 1.63 and 1.22 (m, 1:1 H; 6-H_{eq}, 6-H_{ax}), 1.20 (t, 3H; OCH_2CH_3); ^{13}C NMR (C_6D_6): $\delta = 160.6$ (C_q; C1), 150.1 (C_q; C3), 107.9 (C_q; C3a), 95.0 (CH; C2), 65.3 (OCH_2), 47.2 (CH; C7a), 41.1 (2 NCH_3, dynamically broadened), 32.7 (CH_2; C7), 24.6 (CH_2; C6), 29.0 (CH_2; C4), 26.5 (CH_2; C5), 14.3 (OCH_2CH_3); MS (70 eV): *m*/*z* (%): 207 (50) $[M]^+$, 178 (90) $[M-Et]^+$.



Pentacarbonyl(pyridine)tungsten: ^{1}H NMR (C_6D_6): $\delta = 8.15$ (m, 2H), 6.65 (m, 1H), 6.05 (m, 2H); ^{13}C NMR (C_6D_6): $\delta = 202.4$ and 199.3 (C_q; *trans*- and *cis*-CO of $W(CO)_5$), 155.7, 137.0 and 125.4 (2:1:2, CH); IR (hexane): $\tilde{\nu} =$ 2072 (10), 1932 cm^{-1} (100) (C≡O).

4-(Cyclohex-1-enyl)-2-ethoxy-4-pyrrolidino-1-pentacarbonyltungsta-1,3-butadiene [(3*E*)-5b] and 3-ethoxy-1-pyrrolidino-4,5,6,7-tetrahydro-7a*H*-indene (7b): Compound **1** (243 mg, 0.50 mmol) was treated with pyrrolidine (**2b**) (36 mg, 0.50 mmol) as described above to give complex (3*E*)-**5b** (259 mg, 93 %, $R_f = 0.7$ in *n*-pentane/dichloromethane 2:1, m.p.: 115 °C). Thermolysis of compound (3*E*)-**5b** in the presence of one equivalent of pyridine at 60 °C for 5 h gave compound **7b**.

Data for 5b: ^{1}H NMR (360 MHz, $CDCl_3$, 303 K,): $\delta = 6.23$ (s, 1H; 3-H), 5.55 (m, 1H; 2′-H), 4.51 (m, 2H; OCH_2), 3.43 (m, 4H; 2 NCH_2), 2.10 and 2.03 (m, 2H each; $NCH_2CH_2CH_2$), 2.12 (m, 4H; 3′-H_2, 6′-H_2), 1.91 and 1.74 (m, 2H each; 4′-H_2, 5′-H_2), 1.38 (t, 3H; OCH_2CH_3); ^{13}C NMR ($CDCl_3$): $\delta =$ 265.9 (C_q; C2), 204.2 and 200.9 (C_q; *trans*- and *cis*-CO of $W(CO)_5$), 158.1 (C_q; C4), 136.3 (C_q; C1′), 125.4 (CH; C2′), 120.5 (CH; C3), 76.3 (OCH_2), 49.4 and 49.2 (2 NCH_2), 26.8 and 24.7 (CH_2; C3′, C6′), 25.0 and 24.9 ($NCH_2CH_2CH_2$), 22.2 and 21.5 (CH_2; C4′ and C5′), 15.8 (OCH_2CH_3); IR (diethyl ether): $\tilde{\nu} = 2054.0$ (5), 1959.8 (5), 1920.2 cm^{-1} (100) (C≡O); MS (70 eV ^{184}W): *m*/*z* (%): 557 (1) $[M]^+$, 417 (5) $[M-5\,CO]^+$, 233 (100) $[M-W(CO)_5]^+$; elemental analysis calcd (%) for $C_{20}H_{23}NO_6W$ (557.1): C 43.08, H 4.16, N 2.51; found: C 43.08, H 4.26, N 2.44.

Data for 7b: ^{1}H NMR (C_6D_6): $\delta = 4.95$ (s, 1H; 2-H), 3.92 (m, 2H; diastereotopic OCH_2), 2.91 (m, 4H; 2 NCH_2), 2.63 (dd, $^3J = 5.0$, 11.8 Hz, 1H; 7a-H), 3.07 (m, 1H), 2.31 (m, 1H), 2.06 (m, 1H), 1.76 (m, 2H), 1.27 (m, 1H), 1.15 (m, 2H; 4-H_2–7-H_2), 1.50 (m, 4H; $NCH_2CH_2CH_2$), 1.20 (t, 3H; OCH_2CH_3); ^{13}C NMR (C_6D_6): $\delta = 157.8$ (C_q; C1), 150.9 (C_q; C3), 107.8 (C_q; C3a), 91.9 (CH; C2), 65.3 (OCH_2), 49.2 (2 NCH_2), 48.4 (CH; C7a), 31.7 (CH_2; C7), 28.5 (CH_2; C6), 26.6 (CH_2; C5), 25.4 (2 CH_2; $NCH_2CH_2CH_2$), 24.5 (CH_2; C4), 15.8 (OCH_2CH_3); MS (70 eV): *m*/*z* (%): 233 (50) $[M]^+$, 204 (80) $[M-Et]^+$.

4-(Cyclohex-1-enyl)-2-ethoxy-4-morpholino-1-pentacarbonyltungsta-1,3-butadiene [(3*E*)-5c] and 3-ethoxy-1-morpholino-4,5,6,7-tetrahydro-7a*H*-indene (7c): Compound **1** (243 mg, 0.50 mmol) was treated with morpholine (**2c**) (43 mg, 0.50 mmol) as described above to give compound (3*E*)-**5c** (258 mg, 90 %, $R_f = 0.7$ in *n*-pentane/dichloromethane 2:1, m.p.: 95 °C). A 1:1 mixture of complex (3*E*)-**5c** with pyridine after heating to 60 °C for 1 h gave compound **7c**.

Data for (3*E*)-5c: ^{1}H NMR (C_6D_6, 273 K): $\delta = 6.50$ (s, 1H; 3-H), 5.31 (m, 1H; 2′-H), 4.55 (m, 2H; OCH_2), 3.49 (m, 4H; CH_2OCH_2), 3.06 (m, 4H; 2 NCH_2), 1.76 (m, 4H; 3′-H_2, 6′-H_2), 1.37 (m, 4H; 4′-H_2, 5′-H_2), 1.12 (t, 3H; OCH_2CH_3); ^{13}C NMR (C_6D_6, 273 K): $\delta = 267.7$ (C_q; C2), 204.2 and 200.2 (C_q; *trans*- and *cis*-CO of $W(CO)_5$), 158.9 (C_q; C4), 135.0 (C_q; C1′), 125.9 (CH; C2′), 120.2 (CH; C3), 77.1 (CH_2OCH_2), 76.7 (OCH_2), 50.6 (2 CH_3; $N(CH_3)_2$), 26.4 and 24.6 (CH_2; C3′, C6′), 22.6 and 21.8 (CH_2; C4′, C5′), 15.7 (OCH_2CH_3); IR (hexane): $\tilde{\nu} = 2058.2$ (5), 1923.2 cm^{-1} (100) (C≡O); MS (70 eV, ^{184}W): *m*/*z* (%): 573 (1) $[M]^+$, 517 (30) $[M-3\,CO]^+$, 249 (100) $[M-W(CO)_5]^+$; elemental analysis calcd (%) for $C_{20}H_{23}NO_7W$ (573.3): C 41.90, H 4.04, N 2.44; found: C 41.60, H 4.24, N 2.65.

Data for 7c: ^{1}H NMR (C_6D_6): $\delta = 5.11$ (s, 1H; 2-H), 3.86 (m, 2H; OCH_2), 3.50 (m, 4H; CH_2OCH_2), 3.19 (t, $^3J = 7.0$ Hz, 1H; 7a-H), 2.61 (m, 4H; 2 NCH_2), 3.05 (m, 1H), 2.52 (m, 1H), 2.02 (m, 2H), 1,70 (m, 2H), 1.40 (m, 1H) 1.10 (m, 1H; 4-H_2–7-H_2), 1.19 (t, 3H; OCH_2CH_3); ^{13}C NMR (C_6D_6): $\delta = 160.6$ (C_q; C1), 149.5 (C_q; C3), 109.7 (C_q; C3a), 97.6 (CH; C2), 66.5 (CH_2OCH_2), 65.5 (OCH_2CH_3), 49.7 (2 NCH_2), 46.5 (CH; C7a), 33.1 and 28.2 (CH_2; C7, C6), 26.4 and 24.6 (CH_2; C4, C5), 15.7 (OCH_2CH_3); MS (70 eV): *m*/*z* (%): 249 (50) $[M]^+$, 220 (80) $[M-Et]^+$.

4-(Cyclohex-1-enyl)-2-ethoxy-4-[(2*S*)-2-(methoxymethyl)pyrrolidino-*N*]-1-pentacarbonyltungsta-1,3-butadiene [(3*E*)-5d], (7a*S*)- and (7a*R*)-3-ethoxy-1-[(2S)-2-(methoxymethyl)pyrrolidino-*N*)-4,5,6,7-tetrahydro-7a*H*-indene (7d and 7d′): (2*S*)-(−)-2-(Methoxymethyl)pyrrolidine (**2d**) (58 mg, 0.50 mmol) was treated with **1** (243 mg, 0.50 mmol) as described above to give compound (3*E*)-**5d** (268 mg, 89 %, $R_f = 0.6$ in *n*-pentane/diethyl ether 3:1, yellow crystals, decomp: 91 °C). Thermolysis of compound (3*E*)-**5d** in the presence of one equivalent of pyridine at 60 °C for 3 h gave a 4:1 mixture of compounds **7d** and **7d′**.

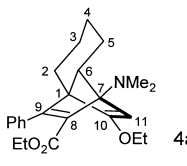
Data for (3*E*)-5d: ^{1}H NMR (400 MHz, $CDCl_3$ at 263 K, freshly prepared sample, minor signals of isomers resulting from hindered rotation of the C4–N bond are given in square brackets): $\delta = 6.40$ [6.20] (s, 1H; 3-H), 5.50 [5.61] ("s", 1H; 2′-H), 4.50 [4.48] (m, 2H; diastereotopic 2-OCH_2), 4.06 [3.86] (t, 1H; NCH), 3.60–3.30 [3.60–3.30] (m, 4H; diastereotopic 2″-CH_2O, CH_2N), 3.27 [3.24] (3H; OCH_3), 2.3–1.6 [2.3–1.6] (12H; 3″-H_2, 4″-H_2, 3′-H_2–6′-H_2), 1.40 [1.39] (t, 3H; OCH_2CH_3); ^{13}C NMR ($CDCl_3$ at

263 K, signals of four equilibrating stereoisomers are detected. Signals of the minor isomers are given in square brackets): $\delta = 265.4$ [267.2, 265.2, 264.3] (C_q; W=C), 204.3 [204.5] and 199.6 [199.6] (C_q; *trans*- and *cis*-CO of $W(CO)_5$], 157.9 [158.3, 157.3] (C_q dynamically broadened; C4), 135.6 [136.3,135.9, 134.7] (br, C_q; C1′), 123.9 [126.5, 125.6, 125.2] (br, CH; C2′), 120.6 [120.1, 119.7] (br, CH; C3), 76.3 [76.2] (2-OCH_2), 73.1 [69.7] (2″-CH_2O], 58.9 [58.5] (OCH_3), 58.7 [58.3] (NCH), 49.9 [49.7, 48.7] (br, NCH_2), 28.8 [28.6] and 28.6 [28.4] (br, CH_2; C3″, C4″), 27.0 [26.9] (CH_2; C3′), 24.3 [24.4, 24.2] (CH_2; C6′), 22.6 [21.9] and 21.1 [21.0] (CH_2; C-4′, C-5′), 15.7 [15.7] (OCH_2CH_3); IR (hexane): $\tilde{\nu} = 2055.8$ (15), 1959.1 (10), 1922.5 cm^{-1} (100) (C≡O); MS (70 eV, ^{184}W): *m*/*z* (%): 601 (10) $[M]^+$, 545 (10) $[M - 2CO]^+$, 517 (30) $[M - 3CO]^+$, 461 (20) $[M - 5CO]^+$, 277 (100) [ligand]; X-ray crystal structure analysis (code AUM323): formula $C_{22}H_{27}NO_7W$, $M = 601.30$, yellow crystal $0.20 \times 0.15 \times 0.10$ mm, $a = 9.783(1)$, $b = 10.650(2)$, $c = 11.532(2)$ Å, $\beta = 99.06(1)°$, $V = 1186.5(3)$ $Å^3$, $\rho_{calcd} = 1.683$ $g\,cm^{-3}$, $\mu = 49.08$ cm^{-1}, empirical absorption correction from ψ scan data ($0.440 \le T \le 0.640$), $Z = 2$, monoclinic, space group $P2_1$ (No. 4), $\lambda = 0.71073$ Å, $T = 293$ K, $\omega/2\theta$ scans, 2697 reflections collected ($+h, -k, \pm l$), $[(\sin\theta)/\lambda] = 0.62$ $Å^{-1}$, 2548 independent ($R_{int} = 0.022$) and 2238 observed reflections [$I \ge 2\sigma(I)$], 282 refined parameters, $R = 0.020$, $wR^2 = 0.048$, max/min residual electron density 0.76/ − 0.59 e $Å^{-3}$, Flack parameter − 0.00(2); disorder at C63, C64, and C65, no adequate model for description found; hydrogens calculated and refined as riding atoms.[25]

Data for 7d {7d′}: ^1H NMR (C_6D_6): $\delta = 5.10$ {5.07} (s, 1H; 2-H), 3.89 {3.88} (m, 2H; OCH_2), 3.60 {3.60} (m, 1H; NCH), 3.42 {3.59} (dd, $J = 3.5$, 9.2 Hz, 2H; OCH_2), 3.16 and 2.82 {3.16 and 2.82} (m, 1H each; NCH_2), 3.12 {3.10} (s, 3H; OCH_3), 2.69 {2.62} (dd, $J = 5.0$, 11.6 Hz, 1H; 7a-H), 3.04 {3.04} (m, 1H), 2.29 {2.29} (m, 1H), 2.05 {2.05} (m, 1H), 1.70 {1.70} (m, 5H), 1.45 {1.45} (m, 1H), 1.20 {1.20} (m, 2H), and 1.10 {1.10} (m, 1H) (4-H_2 to 7-H_2 and 2 CH_2 pyrrolidino), 1.18 {1.19} (t, 3H; OCH_2CH_3); ^{13}C NMR (C_6D_6): $\delta =$ 157.4 {157.4} (C_q; C1), 150.6 {150.6} (C_q; C3), 106.4 {106.1} (C_q; C3a), 92.9 {93.1} (CH; C2), 73.7 {73.4} (CH_2OCH_3), 65.3 {65.3} (3-OCH_2), 60.3 {60.0} (NCH), 58.9 {58.7} (OCH_3), 50.4 {49.6} (NCH_2), 48.4 {48.9} (CH; C7a), 32.4 {32.2} (CH_2; C7), 24.6 {23.6} (CH_2; C6), 29.0 {28.3} (CH_2; C4), 26.5 {26.3} (CH_2; C5), 15.8 {15.8} (OCH_2CH_3); MS (70 eV): *m*/*z* (%): 267 (50) $[M]^+$.

(1*R,6*S**,7*S**)-7-Dimethylamino-10-ethoxy-8-ethoxycarbonyl-9-phenyltricyclo[5.2.2.0^{1,6}]undeca-8,10-diene (4a)**: Compound (3*E*)-**5a** (133 mg, 0.25 mmol), ethyl phenylpropiolate **3a** (43 mg, 0.25 mmol), and pyridine (20 mg, 0.25 mmol) in toluene (1 mL) in a 2 mL screw-top vessel was stirred at 60 °C for 2 h to give a 1:1 mixture of compound **4a** and pentacarbonyl(pyridine)tungsten (^1H NMR spectrum in [D_6]benzene). Flash chromatography on silica gel (column 2×10 cm) with 1:1 dichloromethane/*n*-pentane gave a yellow fraction with pentacarbonyl(pyridine)tungsten, which was discarded. Subsequent elution with diethyl ether/dichloromethane/*n*-pentane (1:1:1) afforded compound **4a** (71 mg, 75 %, $R_f = 0.4$ in diethyl ether/dichloromethane/*n*-pentane 1:1:1, colorless crystals from dichloromethane/diethyl ether, m.p.: 83 °C). If compound **7a** was generated by thermolysis of compound (3*E*)-**5a** as described above, and subsequently treated with compound **3a** at 20 °C for 4 h, cycloadduct **4a** was obtained as the only organic product.

Data for 4a: ^1H NMR (600 MHz, C_6D_6): $\delta = 7.51$, 7.17, and 7.08 (m, 2:2:1 H; *o*-, *m*-, *p*-H C_6H_5), 5.26 (s, 1H; 11-H), 3.95 (m, 2H; diastereotopic CO_2CH_2), 3.54 and 3.46 (m, 1H each; diastereotopic 10-OCH_2), 2.77 (dd, $J = 4.3$, 11.2 Hz, 1H; 6-H), 2.64 (br s, 6H; $N(CH_3)_2$), 2.37 (m, 1 H_{eq}) and 1.02 (m, 1 H_{ax}) (2-H_2), 1.78 (m, 1 H_{ax}) and 1.67 (m, 1 H_{eq}) (5-H_2), 1.51 (m, 1 H_{eq}) and 1.39 (m, 1 H_{ax}, 3-H_2), 1.51 (m, 1 H_{eq}) and 0.90 (m, 1 H_{ax}) (4-H_2), 1.07 (t, 3H; 10-OCH_2CH_3) and 0.87 (t, 3H; OCH_2CH_3); ^{13}C NMR (600 Hz, C_6D_6): $\delta = 172.3$ (C_q; C10), 161.7 (C_q; C9), 168.0 (C_q; C=O), 150.4 (C_q; C8), 135.4 (C_q; C_{ipso} C_6H_5), 128.5, 127.9 and 127.6 (2:2:1, *o*-, *m*-, *p*-C; C_6H_5), 101.0 (CH; C11), 85.3 (C_q; C7), 76.9 (CH; C6), 65.7 (10-OCH_2), 60.8 (C_q; C1), 60.0 (OCH_2), 41.2 ($N(CH_3)_2$), 26.3 (CH_2; C5), 24.4 (CH_2; C2), 23.7 and 23.6 (CH_2; C3, C4), 14.5 and 14.5 (OCH_2CH_3); IR (KBr): $\tilde{\nu} = 1711.6$ (100), 1626.8 cm^{-1} (70) ; MS (70 eV): *m*/*z* (%): 381 (45) $[M]^+$, 308 (80) $[M - Et - NMe_2]^+$, 206 (100); elemental analysis calcd (%) for $C_{24}H_{31}NO_3$ (381.5): C 75.56, H 8.19, N 3.67; found: C 75.58, H 8.46, N 3.66.



4a

(1*R,6*S**,7*S**)-7-Dimethylamino-10-ethoxy-8-ethoxycarbonyltricyclo-[5.2.2.0^{1,6}]undeca-8,10-diene (4b) and (1*R**,6*S**,7*S**)-7-dimethylamino-8-ethoxycarbonyltricyclo-[5.2.2.0^{1,6}]undeca-8-ene-10-one (9b)**: A mixture of complex (3*E*)-**5a** (133 mg, 0.25 mmol), ethyl propiolate **3b** (25 mg, 0.25 mmol) and pyridine (20 mg, 0.25 mmol) in C_6D_6 (1 mL) was treated at 60 °C for 2 h as described above to give a 3:4 mixture of norbornadiene **4b** and pentacarbonyl(pyridine)tungsten (^1H NMR analysis). The solvent was replaced by THF, the mixture was then treated with 3 drops of Hcl (2N), stirred for 3 h at 20 °C, and neutralized with aqueous KOH. Extraction with diethyl ether afforded compound **9b** (52 mg, 72 %, $R_f =$ 0.5 in 1:1 dichloromethane/diethyl ether). An attempt to isolate compound **4b** by fast chromatography failed due to the sensitivity of this compound towards hydrolysis on silica gel.

Data for 4b: ^1H NMR (400 MHz, C_6D_6): $\delta = 7.51$ (s, 1H; 9-H), 5.12 (s, 1H; 11-H), 4.05 (m, 2H; diastereotopic OCH_2), 3.46 and 3.39 (m, 1H each; diastereotopic 10-OCH_2), 2.58 (dd, $^4J = 4.3$ Hz, $^3J = 11.3$ Hz, 1H; 6-H), 2.66 (br s, 6H; $N(CH_3)_2$), 2.25 (m, 1H), 1.77 (m, 1H), 1.56 (m, 3H), 1.36 (m, 1H), 1.18 (m, 1H), and 0.93 (m, 1H) (2-H_2 to 5-H_2), 1.04 and 1.03 (t, 3H each; OCH_2CH_3); ^{13}C NMR (400 Hz, C_6D_6): $\delta = 172.9$ (C_q; C10), 166.0 (C_q; C=O), 155.7 (C_q; C8), 158.4 (CH; C9), 100.6 (CH; C11), 85.0 (C_q; C7), 80.6 (CH; C6), 65.7 (10-OCH_2), 60.3 (OCH_2), 58.5 (C_q; C1), 41.1 ($N(CH_3)_2$), 26.0 (CH_2; C5), 24.8 (CH_2; C2), 24.1 and 23.8 (CH_2; C3, C4), 14.6 (2 OCH_2CH_3); IR (KBr): $\tilde{\nu} = 1712.2$ (100), 1626.8 cm^{-1} (70); MS (70 eV): *m*/*z* (%): 305 (20) $[M]^+$, 277 (70) $[M - C_2H_4]^+$, 232 (30) $[M - Et - NMe_2]^+$, 176 (80).

Data for 9b: ^1H NMR (C_6D_6): $\delta = 6.44$ (s, 1H; 9-H), 3.99 (m, 2H; diastereotopic OCH_2), 2.28 (dd, $J = 4.2$, 11.0 Hz, 1H; 6-H), 2.49 (s, 6H; $N(CH_3)_2$), 2.23 (m, 1H) and 2.21 (m, 1H) (10-H_2), 2.12 (m, 1H), 1.745 (m, 4H), 1.30 (m, 2H), 1.05 (m, 1H), and 0.80 (m, 1H) [2-H_2 to 5-H_2], 1.01 (t, 3H; OCH_2CH_3); ^{13}C NMR (C_6D_6): $\delta = 209.7$ (C_q; C11), 164.8 (C_q; *C*(O)OEt), 144.9 (CH; C9), 75.0 (CH; C6), 63.8 and 63.4 (C_q; C1, C7), 60.3 (OCH_2), 40.1 ($N(CH_3)_2$), 38.7 (CH_2; C10), 24.2, 23.8, 23.0 and 22.7 (CH_2; C3 – C5), 14.2 (OCH_2CH_3); IR (KBr): $\tilde{\nu} = 1742.5$ (30), 1714.3 cm^{-1} (100); MS (70 eV): *m*/*z* (%): 277 (60) $[M]^+$, 249 (80) $[M - C_2H_4]^+$, 176 (100); elemental analysis calcd (%) for $C_{16}H_{23}NO_3$ (277.4): C 69.29, H 8.36, N 5.05; found: C 68.81, H 8.21, N 4.90.

(1*R,6*S**,7*S**)-10-Ethoxy-8-ethoxycarbonyl-9-phenyl-7-pyrrolidinotricyclo[5.2.2.0^{1,6}]-undeca-8,10-diene (4c)**: A mixture of 1-tungstahexatriene (3*E*)-**5b** (133 mg, 0.25 mmol), ethyl phenylpropiolate (**3a**) (43 mg, 0.25 mmol), and pyridine (20 mg, 0.25 mmol) in toluene (1 mL) was reacted at 60 °C for 5 h as decribed above to give compound **4c** (79 mg, 78 %, $R_f = 0.4$ in dichloromethane/diethyl ether/*n*-pentane 1:1:2, crystals from diethyl ether/dichloromethane 3:1, m.p.: 87 °C). ^1H NMR (C_6D_6): $\delta =$ 7.46, 7.18 and 7.09 (m, 2:2:1 H; *o*-, *m*, *p*-H C_6H_5), 5.31 (s, 1H; 11-H), 3.90 (m, 2H; diastereotopic OCH_2), 3.55 and 3.51 (mh, 1H each; diastereotopic 10-OCH_2), 3.19 (s, 4H; 2 NCH_2), 2.77 (ddd, $J = 0.8$, 4.4, 11.2 Hz, 1H; 6-H), 1.83 (m, 4H; 2 $NCH_2CH_2CH_2$), 2.35 (m, 1 H_{eq})and 1.03 (m, 1 H_{ax}) (2-H_2), 1.78 (m, 1 H_{ax}) and 1.67 (m, 1 H_{eq}) (5-H_2), 1.51 (m, 1 H_{eq}) and 1.39 (m, 1 H_{ax}) (3-H_2), 1.51 (m, 1 H_{eq}) and 0.92 (m, 1 H_{ax}) (4-H_2), 1.09 (t, 3H; 11-OCH_2CH_3), 0.83 (t, 3H; OCH_2CH_3); ^{13}C NMR (C_6D_6): $\delta = 172.1$ (C_q; C11), 163.1 (C_q; C9), 168.1 (C_q; C=O), 150.4 (C_q; C8), 135.8 (C_q; C_{ipso} C_6H_5), 128.5, 127.9 and 127.5 (2:2:1, *o*-, *m*-, *p*-C; C_6H_5), 101.8 (CH; C11), 82.5 (C_q; C7), 79.1 (CH; C6), 65.6 (10-OCH_2), 61.0 (C_q; C1), 59.8 (OCH_2), 48.9 (2 NCH_2), 26.8 (CH_2; C5), 25.4 ($NCH_2CH_2CH_2$), 24.5 (CH_2; C2), 23.9 and 23.7 (CH_2; C3, C4), 14.5 and 14.1 (OCH_2CH_3); IR (KBr): $\tilde{\nu} = 1707.4$ (100), 1592 cm^{-1} (40); MS (70 eV): *m*/*z* (%): 407 (45) $[M]^+$, 308 (80) $[M - CO_2Et]^+$, 232 (100); elemental analysis calcd (%) for $C_{26}H_{33}NO_3$ (407.6): C 76.62, H 8.16, N 3.44; found: C 76.47, H 8.31, N 3.36; X-ray crystal structure analysis (code AUM1559): formula $C_{26}H_{33}NO_3$, $M = 407.53$, colorless crystal $0.20 \times 0.15 \times$ 0.10 mm, $a = 10.760(2)$, $b = 20.672(3)$, $c = 10.179(2)$ Å, $\beta = 98.98(2)°$, $V =$ 2236.4(7) $Å^3$, $\rho_{calc} = 1.210$ $g\,cm^{-3}$, $\mu = 6.16$ cm^{-1}, empirical absorption correction from ψ-scan data ($0.887 \le T \le 0.941$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 4797 reflections collected ($+h, +k, \pm l$), $[(\sin\theta)/\lambda] = 0.62$ $Å^{-1}$, 4555 independent ($R_{int} =$ 0.036) and 2966 observed reflections [$I \ge 2\sigma(I)$], 273 refined parameters, $R = 0.049$, $wR^2 = 0.115$, max/min residual electron density 0.25/ − 0.25 e $Å^{-3}$; hydrogens calculated and refined as riding atoms.[25]

(1*R*,6*S*,7*S*)- and (1*R*,6*S*,7*S*)-7-[(2*S*)-2-(Methoxymethyl)pyrrolidino]-11-ethoxy-8-ethoxycarbonyl-9-phenyltricyclic[5.2.2.0^{1,6}]undeca-8,10-diene (4d) and (4d′): A mixture of (3*E*)-**5d** (150 mg, 0.25 mmol), ethyl phenylpropiolate (**3a**) (43 mg, 0.25 mmol), and pyridine (20 mg, 0.25 mmol) in toluene (1 mL) was reacted at 60 °C for 5 h as decribed above to give a 7:1 mixture of compounds **4d** and **4d′** together with pentacarbonyl(pyridine)-tungsten as indicated by the NMR spectra. A 4:1 mixture of compounds **4d**

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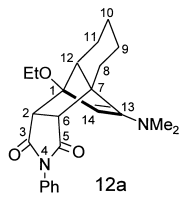
and **4d′** was obtained, if a solution of compound **7d** was generated as described above and subsequently reacted with the alkyne **3a**.

Data for 4d {4d′}: ^{1}H NMR (C_6D_6): $\delta = 7.47$, 7.17, and 7.10 {7.52, 7.25, and 7.1} (m each, 2:2:1 H; Ph), 5.38 {5.40} (s, 1 H; 11-H), 4.04 {4.04} (m, 1 H; NCH), 3.86 {3.86} (m, 2 H; diastereotopic OCH_2), 3.52 and 3.43 {3.52 and 3.43} (m each, 1 H each, 10-OCH_2), 3.55 and 3.08 {3.18 and 3.08} (m, 1 H each; diasterotopic CH_3OCH_2), 3.30 {3.25} (s, 3 H; OCH_3), 3.18 and 3.08 {3.55 and 3.08} (m, 1 H each; diastereotopic NCH_2), 2.61 {2.75} (dd, 1 H; $J = 4.5$, 10.9 Hz, 6-H), 2.30 {2.30} (m, 1 H), 2.05 {2.05} (m, 1 H), 1.80 {1.80} (m, 3 H), 1.55 {1.55} (m, 6 H), and 1.10 {1.10} (m, 1 H) ($NCH_2CH_2CH_2$ and 2-H_2 to 5-H_2), 1.06 {0.95} (t, 3 H; 11-OCH_2CH_3) and 0.81 {0.87} (t, 3 H; OCH_2CH_3); ^{13}C NMR (C_6D_6): $\delta = 172.4$ {172.3} (C_q; C11), 164.8 {162.0} (C_q; C9), 167.5 {167.4} (C_q; C=O), 150.4 {151.0} (C_q; C8), 133.0 {133.0} (C_q; C_{ipso} C_6H_5), 128.8, 127.8, and 127.6 {128.8, 127.8, and 127.6} (2:2:1; Ph), 101.6 {101.9} (CH; C11), 83.2 {83.7} (C_q; C7), 78.5 {78.4} (CH_3OCH_2), 78.2 {78.3} (CH; C6), 65.7 {65.7} (10-OCH_2), 61.1 {61.2} (C_q; C1), 59.9 {59.9} (OCH_2), 59.6 {59.8} (NCH), 58.9 {58.8} (OCH_3), 49.8 {50.8} (NCH_2), 30.1 {29.9} (CH_2; C3′), 24.7, 24.6, 24.4, 24.1, and 23.7 {25.5, 24.9, 24.0, and 23.8} (CH_2; C4′, and C2 to C5), 14.5 and 14.0 {14.5 and 14.1} (OCH_2CH_3); IR (KBr), $\tilde{\nu} = 1707.4$ (100), 1592.1 cm^{-1} (30); MS (70 eV): *m/z* (%): 451 (70) $[M]^+$, 422 (50) $[M - Et]^+$.

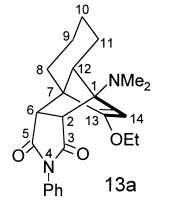
(1*S,2*R**,6*S**,7*R**,12*S**)-*N*-Phenyl-4-aza-13-dimethylamino-1-ethoxytetracyclo[5.5.2.0^{2,6}.0^{7,12}]tetradeca-13-ene-3,5-dione (12a) and (1*S**,2*R**,6*S**,7*R**,12*S**)-*N*-phenyl-4-aza-1-dimethylamino-13-ethoxytetracyclo[5.5.2.0^{2,6}.0^{7,12}]tetradeca-13-ene-3,5-dione (13a)**: 1-Tungsta-1,3,5-hexatriene (3*E*)-**5a** (133 mg, 0.25 mmol), *N*-phenyl maleimide **11** (81 mg, 0.25 mmol), and pyridine (20 mg, 0.25 mmol) were reacted as described above at 60 °C for 2 h to give the [4+2] cycloadduct **12a** in smooth reaction according to the NMR spectrum of the reaction mixture. Compound **12a** was isolated by evaporation of the solvent, washing of the residue with *n*-pentane/diethyl ether 4:1 in order to remove pentacarbonyl(pyridine)tungsten and crystallization from dichloromethane/diethyl ether (61 mg, 64 %, m.p.: 135 °C). If the cyclopentadiene **7a** was generated as described above and subsequently reacted with the dienophile **11** at 20 °C, the [4+2] cycloadduct **13a** was obtained within a few minutes (81 mg, 85 %, $R_f = 0.5$ in dichloromethane/diethyl ether 1:1, crystals from diethyl ether/dichloromethane 3:1, m.p.: 139 °C).

Data for 12a: ^{1}H NMR (C_6D_6): $\delta = 7.39$, 7.18, and 7.10 (m, 2:2:1 H; C_6H_5), 4.67 (s, 1 H; 14-H), 3.32 and 3.35 (m, 1 H each; diastereotopic OCH_2), 3.23 (d, $^3J = 8.2$ Hz, 1 H; 2-H), 2.61 (d, 1 H; $J = 8.4$ Hz, 6-H), 2.48 (s, 6 H; $2N(CH_3)_2$), 2.45 (m, 1 H; 12-H), 2.73 (m, 1 H), 2.45 (m, 1 H), 1.53 (m, 2 H), 1.42 (m, 2 H), 1.25 (m, 1 H), and 0.87 (m, 1 H) (8-H_2 to 11-H_2), 0.96 (t, 3 H; OCH_2CH_3); ^{13}C NMR (C_6D_6): $\delta =$ 176.2 and 174.6 (C_q C3, C5), 160.2 (C_q; C13), 133.5 (C_q; C_{ipso} C_6H_5), 128.7 and 126.4 (2:1:2, *m*-, *p*-, *o*-C; C_6H_5), 95.2 (CH; C14), 80.6 (C_q; C1), 65.0 (OCH_2), 62.8 (CH; C12), 55.0 (C_q; C7), 52.9 (CH; C6), 46.0 (CH; C2), 40.3 ($N(CH_3)_2$), 27.5 (CH_2; C8), 24.2 (CH_2; C11), 23.6 and 22.2 (CH_2; C9, C10), 14.2 (OCH_2CH_3); IR (KBr): $\tilde{\nu} = 1708.7$ (100), 1605.9 cm^{-1} (30); MS (70 eV): *m/z* (%): 380 (10) $[M]^+$, 207 (100) $[M - C_{10}H_7NO_2]^+$; elemental analysis calcd (%) for $C_{23}H_{28}N_2O_3$ (380.5): C 72.61, H 7.42, N 7.36; found: C 72.41, H 7.37, N 7.11.



12a

Data for 13a: ^{1}H NMR (600 Hz, C_6D_6): $\delta = 7.34$, 7.23, and 7.10 (m each, 2:2:1 H; C_6H_5), 4.59 (s, 1 H; 14-H), 3.84 and 3.72 (m, 1 H each; diastereotopic OCH_2), 3.28 (d, $J = 8.3$ Hz, 1 H; 2-H), 2.77 (d, $^3J = 8.4$ Hz, 1 H; 6-H), 2.43 (brs, 6 H; 2 $N(CH_3)_2$), 1.62 (m, 1 H; 12-H), 2.67 (m, 1 H_{eq}) and 1.16 (m, 1 H_{ax}) (8-H_2), 1.60 (m, 1 H_{ax}) and 1.48 (m, 1 H_{eq}) (11-H_2), 1.39 (m, 1 H_{eq}) and 1.28 (m, 1 H_{ax}) (9-H_2), 1.48 (m, 1 H_{eq}) and 0.86 (m, 1 H_{ax}) (10-H_2), 1.27 (t, 3 H; OCH_2CH_3); ^{13}C NMR (600 Hz, C_6D_6): $\delta = 175.8$ and 175.5 (C_q; C3, C5), 150.3 (C_q; C13), 133.3 (C_q; C_{ipso} C_6H_5), 128.8, 128.1, and 127.0 (2:1:2, CH; C_6H_5), 97.8 (CH; C14), 92.2 (C_q; C1), 67.6 (CH; C12), 61.0 (OCH_2), 55.6 (C_q; C7), 53.8 (CH; C6), 50.8 (CH; C2), 41.0 ($N(CH_3)_2$), 32.4 (CH_2; C8), 24.4 (CH_2; C11), 23.5 and 22.9 (CH_2; C9, C10), 16.1 (OCH_2CH_3); IR (KBr): $\tilde{\nu} = 1708.7$ (100), 1591.9 cm^{-1} (30); MS (70 eV): *m/z* (%): 380 (10) $[M]^+$, 207 (100) $[M - C_{10}H_7NO_2]^+$; elemental analysis calcd (%) for $C_{23}H_{28}N_2O_3$ (380.5): C 72.61, H 7.42, N 7.36; found: C 72.52, H 7.09, N 7.31.

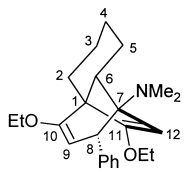


13a

(1*S*,2*R*,6*S*,7*R*,12*S*)-*N*-Phenyl-4-aza-13-[(2*S*)-2-(methoxymethyl)pyrrolidino)]-1-ethoxytetracyclo[5.5.2.0^{2,6}.0^{7,12}]tetradeca-13-en-3,5-dione (12d): Compound (3*E*)-**5d** (150 mg, 0.25 mmol), *N*-phenyl maleimide **11** (43 mg, 0.25 mmol), and pyridine (20 mg, 0.25 mmol) in [D_6]benzene (1 mL) at 60 °C for 2 h was smoothly transformed into a 1:1 mixture of compound **12d** and pentacarbonyl(pyridine)tungsten (NMR spectrum). Fast chromatography on silica gel (column 2 × 10 cm) with dichloromethane/diethyl ether/*n*-pentane 1:1:1 gave (yellow) pentacarbonyl(pyridine)tungsten and the cycloadduct **12d** (91 mg, 81 %, $R_f = 0.3$ in dichloromethane/diethyl ether/*n*-pentane 1:1:1, yellowish crystals from diethyl ether/dichloromethane 3:1, m.p.: 131 °C). ^{1}H NMR (400 Hz, C_6D_6): $\delta = 7.36$, 7.14 and 7.03 (m, 2:2:1 H; *o*-, *m*- and *p*-H C_6H_5), 4.64 (s, 1 H; 14-H), 3.79 and 3.84 (m, 1 H each; diastereotopic OCH_2CH_3), 3.45 (m, 1 H; NCH), 3.45 and 3.15 (m, 1 H each; diastereotopic CH_2OMe), 3.36 and 3.15 (m, 1 H each; diastereotopic NCH_2), 3.17 (d, $J = 8.4$ Hz, 1 H; 2-H), 3.04 (s, 3 H; OCH_3), 2.64 (d, $J =$ 8.4 Hz, 1 H; 6-H), 2.76 (m, 1 H_{eq}) and 1.21 (m, 1 H_{ax}) (8-H_2), 1.59 (m, 2 H_{ax}) and 1.46 (m, 1 H_{eq}) (11-H_2), 1.53 (m, 1 H; 12-H), 1.48 (m, 1 H_{eq}) and 1.29 (m, 1 H_{ax}) (9-H_2), 1.44 (m, 1 H_{eq}) and 0.96 (m, 1 H_{ax}) (10-H_2), 1.56 and 1.49 (3′-H_2, 4′-H_2), 1.28 (t, 3 H; OCH_2CH_3); ^{13}C NMR (400 Hz, C_6D_6): $\delta = 176.0$ and 175.3 (C_q; C3, C5), 147.3 (C_q; C13), 133.4 (C_q; C_{ipso} C_6H_5), 128.8, 127.9, and 126.8 (2:1:2, *m*-, *p*-, *o*-C; C_6H_5), 93.3 (CH; C14), 92.2 (C_q; C1), 71.6 (CH_3OCH_2), 67.0 (CH; C12), 61.0 (2 C; OCH_2, NCH), 58.7 (OCH_3), 55.9 (C_q; C7), 54.0 (CH; C6), 50.8 (CH; C2), 48.7 (NCH_2), 32.1 (CH_2; C8), 28.6 (CH_2; C3′), 24.7 and 24.6 (CH_2; C11, C4′), 23.7 and 23.1 (CH_2; C9, C10), 16.2 (OCH_2CH_3); IR (KBr): $\tilde{\nu} = 1709.1$ (100), 1591.2 cm^{-1} (30); MS (70 eV): *m/z* (%): 450 (10) $[M]^+$, 277 (100) $[M - C_{10}H_7NO_2]^+$; $[\alpha]_D^{20} = 57°$ (in CH_2Cl_2); elemental analysis calcd (%) for $C_{27}H_{34}N_2O_4$ (450.6): C 71.97, H 7.61, N 6.22; found: C 71.72, H 7.45, N 6.09.

(1*R,6*S**,7*R**,8*S**)-7-Dimethylamino-10,11-diethoxy-8-phenyltricyclo[5.3.2.0^{1,6}]dodeca-9,11-diene (15a)**: 1-Tungsta-1,3,5-hexatriene (3*E*)-**5a** (133 mg, 0.25 mmol), (3*E*)-4-phenyl-1-tungsta-1,3-butadiene (**14a**) (121 mg, 0.25 mmol) and pyridine (20 mg, 0.25 mmol) were reacted as described above in toluene (1 mL) in a 2 mL screw-top vessel at 60 °C for 3 h. Flash chromatography on silica gel (column 2 × 10 cm) with dichloromethane/*n*-pentane (1:1) afforded a yellow band with pentacarbonyl(pyridine)tungsten, which was discarded. Subsequent elution with diethyl ether/dichloromethane/*n*-pentane (1:1:1) gave compound **15a** (67 mg, 74 %, $R_f =$ 0.7 in diethyl ether/dichloromethane/*n*-pentane 1:1:1, colorless crystals, m.p.: 61 °C). Reaction of compound (3*E*)-**5a** with (3*E*)-4-phenyl-1-chroma-1,3-butadiene **14b** as described above produced compound **15a** in 72 % isolated yield. Cyclopentadiene **7a**, prepared as described above, was treated with complex **14a** at 20 °C for 5 h to also generate compound **15a**. Isolation of compound **15a** by fast chromatography on silica gel (ca. 20 min) was possible, but involved substantial loss of yield by hydrolysis to give compound **16a**.

Data for 15a: ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.40$, 7.28, and 7.17 (m, 2:2:1 H; C_6H_5), 4.27 (d, $J = 3.2$ Hz, 1 H; 9-H), 4.11 (s, 1 H; 12-H), 4.06 (d, $J = 3.2$ Hz, 1 H; 8-H), 3.58 and 3.53 (m, 1 H each; diastereotopic 10-OCH_2), 3.43 and 3.40 (m, 1 H each; diastereotopic 11-OCH_2), 2.43 (brs, 6 H; $N(CH_3)_2$), 2.33 (dd, $J = 5.1$, 11.2 Hz, 1 H; 6-H), 2.64 and 1.53 (m, 1 H each; 2-H_2), 1.68 and 1.33 (m, 1 H each; 3-H_2), 1.62 (m, 2 H; 5-H_2), 1.64 and 1.12 (m, 1 H each; 4-H_2), 1.07 and 1.06 (t, 3 H each; OCH_2CH_3); ^{13}C NMR (400 Hz, C_6D_6): $\delta = 164.7$ (C_q; C10), 162.5 (C_q; C11), 143.8 (C_q; C_{ipso} C_6H_5), 130.2, 127.6, and 126.4 (2:2:1, *o*-, *m*-, *p*-C; C_6H_5), 98.0 (CH; 9-H), 93.6 (CH; C12), 73.4 (C_q; C7), 64.9 (10-OCH_2), 62.3 (11-OCH_2), 56.8 (CH; C6), 51.1 (C_q; C1), 45.6 (CH; C8), 39.1 (CH_3 dynamically broadened; $N(CH_3)_2$), 26.5 (CH_2; C5), 25.0 (CH_2; C4), 24.2 (CH_2; C2), 23.3 (CH_2; C3), 14.5 (10- and 11-OCH_2CH_3); MS (70 eV): *m/z* (%): 367 (5) $[M]^+$, 238 (30) $[M - C_2H_9]^+$, 131 (100); elemental analysis calcd (%) for $C_{24}H_{33}NO_2$ (367.5): C 78.43, H 9.05, N 3.81; found: C 78.22, H 8.89, N 3.78.



15a

(1*R,6*S**,7*R**,8*S**)-7-Dimethylamino-10,11-diethoxy-8-(2-thienyl)-tricyclo[5.3.2.0^{1,6}]-dodeca-9,11-diene (15b)**: A one-pot three-component reaction

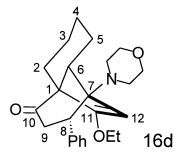
of compound (3*E*)-**5a** (133 mg, 0.25 mmol), (3*E*)-4-(2-thienyl)-1-tungsta-1,3-butadiene (**14c**) (122 mg, 0.25 mmol), and pyridine (20 mg, 0.25 mmol) in toluene (1 mL) as described above gave compound **15b** (66 mg, 71%, $R_f = 0.7$ in diethyl ether/dichloromethane/*n*-pentane 1:1:1, colorless oil). ^{1}H NMR (C_6D_6): $\delta = 7.04$ and 6.90 (dd, 1H each; 3-H, 5-H, 2-thienyl), 6.97 (m, 1H; 4-H, 2-thienyl), 4.37 (d, $J = 2.8$ Hz, 1H; 9-H), 4.30 (d, $J = 2.8$ Hz, 1H; 8-H), 4.18 (s, 1H; 12-H), 3.58 and 3.53 (m, 1H each; diastereotopic 10-OCH_2), 3.45 and 3.42 (m, 1H each; diastereotopic 11-OCH_2), 2.50 (br s, 6H; $N(CH_3)_2$), 2.27 (dd, $J = 4.6$, 10.4 Hz, 1H; 6-H), 2.60 (m, 1H), 1.63 (m, 4H), 1.48 (m, 1H), 1.27 (m, 1H), and 1.12 (m, 1H) (2-H_2 – 5-H_2), 1.07 and 1.02 (t, 3H each; OCH_2CH_3 each); ^{13}C NMR (C_6D_6): $\delta = 165.8$ (C_q; C10), 163.0 (C_q; C12), 147.0 (C_q; C2, 2-thienyl), 125.5, 124.8, and 124.3 (C_q; C3, C4, and C5, 2-thienyl), 97.2 (CH; 9-H), 94.2 (CH; C12), 73.2 (C_q; C7), 65.1 (10-OCH_2), 62.6 (11-OCH_2), 56.1 (CH; C6), 51.5 (C_q; C1), 41.9 (CH; C8), 39.1 (2CH_3 dynamically broadened; $N(CH_3)_2$), 26.8 (CH_2; C5), 24.9 (CH_2; C4), 24.0 (CH_2; C2), 23.3 (CH_2; C3), 14.4 (10-, 11-OCH_2CH_3); MS (70 eV): *m*/*z* (%): 373 (15) $[M]^+$, 344 (100) $[M - Et]^+$; elemental analysis calcd (%) for $C_{22}H_{31}NO_2S$ (373.6): C 70.74, H 8.36, N 3.75; found: C 70.62, H 8.20, N 3.79.

(1*R,6*S**,7*R**,8*S**)-7-Dimethylamino-10,11-diethoxy-8-[(1*E*)-phenylethenyl]-tricyclo[5.3.2.0^{1,6}]dodeca-9,11-diene (15c)**: Reaction of compound (3*E*)-**5a** (133 mg, 0.25 mmol) with **14d** (127 mg, 0.25 mmol) and pyridine (20 mg, 0.25 mmol) in toluene (1 mL) as described above gave compound **15c** (50 mg, 53%, $R_f = 0.7$ in diethyl ether/dichloromethane/*n*-pentane 1:1:1,colorless oil). ^{1}H NMR (400 MHz, C_6D_6/CS_2 1:1): $\delta = 7.23$, 7.14, and 7.02 (m, 2:2:1H; C_6H_5), 6.37 (d, $J = 15.9$ Hz, 1H; 2′-H), 6.26 (dd, $J = 7.8$, 15.9 Hz, 1H; 1′-H), 4.25 (s, 1H; 12-H), 3.99 (d, $J = 2.8$ Hz, 1H; 9-H), 3.54 (dd, $J = 2.8$, 7.8 Hz, 1H; 8-H), 3.62 and 3.60 (m, 1H each; diastereotopic 10-OCH_2), 3.48 and 3.45 (m, 1H each; diastereotopic 11-OCH_2), 2.45 (br s, 6H; $N(CH_3)_2$), 2.11 (ddd, $J = 1.0$, 4.9, 11.0 Hz, 1H; 6-H), 2.29 and 1.54 (m, 1H each; 2-H_2), 1.70 and 1.34 (m, 1H each; 3-H_2), 1.71 and 1.65 (m, 2H; 5-H_2), 1.69 and 1.11 (m, 1H each; 4-H_2), 1.14 and 1.13 (t, 3H each; OCH_2CH_3); ^{13}C NMR (400 Hz, C_6D_6): $\delta = 165.5$ (C_q; C10), 162.8 (C_q; C11), 138.9 (C_q; C_{ipso} C_6H_5), 132.6 (CH; C1′), 131.3 (CH; C2′), 128.8, 126.8, and 126.4 (2:1:2, CH; C_6H_5), 95.4 (CH; 9-H), 92.8 (CH; C11), 72.4 (C_q; C7), 64.9 (10-OCH_2), 62.5 (11-OCH_2), 55.5 (CH; C6), 51.1 (C_q; C1), 43.1 (CH; C8), 39.9 (2CH_3 dynamically broadened; $N(CH_3)_2$), 26.5 (CH_2; C9), 25.3 (CH_2; C4), 24.2 (CH_2; C2), 23.5 (CH_2; C3), 14.8 and 14.7 (10-, 12-OCH_2CH_3); MS (70 eV): *m*/*z* (%): 393 (15) $[M]^+$, 364 (100) $[M - Et]^+$; elemental analysis calcd (%) for $C_{26}H_{35}NO_2$ (380.5): C 79.35, H 8.96, N 3.56; found: C 79.25, H 9.30, N 3.26.

(1*R,6*S**,7*R**,8*S**)-10,11-Diethoxy-7-morpholino-8-phenyltricyclo-[5.3.2.0^{1,6}]dodeca-9,11-diene (15d) and (1*R**,6*S**,7*R**,8*S**)-11-ethoxy-7-morpholino-8-phenyltricyclo-[5.3.2.0^{1,6}]dodeca-11-en-10-one (16d)**: A one-pot three-component reaction of compound (3*E*)-**5c** (143 mg, 0.25 mmol), **14a** (121 mg, 0.25 mmol) and pyridine (20 mg, 0.25 mmol) in toluene (1 mL) as described above gave compound **15d** (55 mg, 56%, $R_f =$ 0.7 in diethyl ether/dichloromethane/*n*-pentane 1:2:4, colorless crystals from dichloromethane/diethyl ether, m.p.: 134 °C). A small fraction that contained compound **16d** (16 mg, 17%, $R_f = 0.6$ in 1:2:4 diethyl ether/dichloromethane/*n*-pentane 1:2:4, colorless crystals, m.p.: 156 °C) was also obtained.

Data for 15d: ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.40$, 7.27, and 7.18 (m, 2:2:1H; C_6H_5), 4.23 (d, $J = 2.2$ Hz, 1H; 9-H), 4.04 (s, 1H; 12-H), 4.00 (d, $J = 2.2$ Hz, 1H; 8-H), 3.62 and 3.53 (m, 1H each; diastereotopic 10-OCH_2), 3.52 (br s, 4H; CH_2OCH_2), 3.38 (m, 2H; diastereotopic 11-OCH_2), 2.78 and 2.51 (br s, 2H each; NCH_2), 2.27 (dd, $J = 6.4$ and 10.8 Hz, 1H; 6-H), 2.65 and 1.53 (m, 1H each; 2-H_2), 1.68 and 1.32 (m, 1H each; 3-H_2), 1.57 (m, 2H; 5-H_2), 1.60 and 1.04 (m, 1H each; 4-H_2), 1.09 and 1.06 (t, 3H each; OCH_2CH_3 each); ^{13}C NMR (400 Hz, C_6D_6): $\delta = 165.0$ (C_q; C10), 162.2 (C_q; C12), 143.1 (C_q; C_{ipso} C_6H_5), 130.5, 127.7, and 126.6 (2:2:1, CH each; C_6H_5), 98.3 (CH; 9-H), 92.3 (CH; C12), 73.4 (C_q; C7), 68.1 (CH_2OCH_2 dynamically broadened), 65.0 (10-OCH_2), 62.5 (11-OCH_2), 56.3 (CH; C6), 51.1 (C_q; C1), 47.0 (dynamically broadened 2NCH_2), 45.9 (CH; C8), 26.5 (CH_2; C5), 25.0 (CH_2; C4), 24.2 (CH_2; C2), 23.3 (CH_2; C3), 14.5 (10-, 11-OCH_2CH_3); MS (70 eV): *m*/*z* (%): 409 (10) $[M]^+$, 380 (100) $[M - C_2H_5]^+$; elemental analysis calcd (%) for $C_{26}H_{35}NO_3$ (409.6): C 76.25, H 8.61, N 3.42; found: C 76.62, H 8.53, N 3.31; X-ray crystal structure analysis (code AUM1615): formula $C_{26}H_{35}NO_3$, $M = 409.55$, light yellow crystal $0.30 \times 0.07 \times 0.03$ mm, $a =$ 9.031(1), $b = 10.395(1)$, $c = 23.580(1)$ Å, $\beta = 96.07(1)°$, $V = 2201.2(3)$ Å^3, $\rho_{calcd} = 1.236$ g cm^{-3}, $\mu = 0.80$ cm^{-1}, absorption correction from SORTAV ($0.977 \le T \le 0.998$), $Z = 4$, monoclinic, space group $P2_1/R$ (No. 14), $\lambda =$ 0.71073 Å, $T = 198$ K, ω and ϕ scans, 14298 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.59$ Å^{-1}, 3882 independent ($R_{int} = 0.101$) and 2254 observed reflections [$I \ge 2\sigma(I)$], 274 refined parameters, $R = 0.058$, $wR^2 =$ 0.097, max/min residual electron density 0.19/ – 0.21) e Å^{-3}, hydrogens calculated and refined as riding atoms.[25]

Data for 16d: ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.17$ (m, 5H; *o*-, *m*-, *p*-H C_6H_5), 4.77 (s, 1H; 12-H), 3.50 (m, 2H; diastereotopic OCH_2), 3.48 and 3.32 (br s, 2H each; CH_2OCH_2), 3.20 (dd, $J = 3.2$, 10.9 Hz, 1H; 8-H), 2.78 (dd, $J = 10.3$, 16.9 Hz, 1H) and 2.56 (dd, $J = 6.5$, 17.0, 1H) (9-H_2), 2.72 and 2.22 (br s, 2H each; NCH_2), 1.90 (dd, $J =$ 5.5, 10.8 Hz, 1H; 6-H), 2.35 and 1.80 (m, 1H each; 2-H_2), 1.61 and 1.20 (m, 1H each; 3-H_2), 1.61 and 1.47 (m, 1H each; 5-H_2), 1.52 and 0.95 (m, 1H each; 4-H_2), 1.06 (t, 3H; OCH_2CH_3); ^{13}C NMR (400 Hz, C_6D_6): $\delta = 206.4$ (C_q; C10), 160.29 (C_q; C12), 143.8 (C_q; C_{ipso} C_6H_5), 128.8, 128.6, and 127.1 (2:2:1, CH each; C_6H_5), 96.7 (CH; C12), 73.2 (C_q; C7), 67.3 (dynamically broadened CH_2OCH_2), 65.4 (11-OCH_2), 61.7 (C_q; C1), 55.5 (CH; C6), 48.7 (CH; C8), 46.0 (CH_2; C9), 45.6 (dynamically broadened 2NCH_2), 26.8 (CH_2; C5), 25.6 (CH_2; C4), 23.5 (CH_2; C2), 23.0 (CH_2; C3), 14.3 (OCH_2CH_3); IR (KBr): $\tilde{\nu} = 1707.9$ (100), 1631.5 cm^{-1} (40); MS (70 eV): *m*/*z* (%): 381 (20) $[M]^+$, 248 (100); elemental analysis calcd (%) for $C_{24}H_{31}NO_3$ (381.5): C 75.56, H 8.19, N 3.67; found: C 75.48, H 8.12, N 3.52.



(1*R,6*S**,7*R**,8*S**)-10,11-Diethoxy-7-morpholino-8-(2-thienyl)-tricyclo-[5.3.2.0^{1,6}]dodeca-9,11-diene (15e) and (1*R**,6*S**,7*R**,8*S**)-11-ethoxy-7-morpholino-8-(2-thienyl)-tricyclo[5.3.2.0^{1,6}]dodeca-11-en-10-one (16e)**: The one-pot three-component reaction of compound (3*E*)-**5c** (143 mg, 0.25 mmol) and **14c** (122 mg, 0.25 mmol) with pyridine (20 mg, 0.25 mmol) in toluene (1 mL) as described above gave compound **15e** (51 mg, 53%, $R_f = 0.7$ in diethyl ether/dichloromethane/*n*-pentane 1:2:6, colorless crystals from dichloromethane/diethyl ether, m > p > : 112 °C). Even fast chromatography on silica gel with *n*-pentane/dichloromethane/diethyl ether (8:4:1) leads to partial hydrolysis to give ketone **16e** (16 mg, 17%, $R_f = 0.5$ in diethyl ether/dichloromethane/*n*-pentane 1:2:6, colorless crystal, m.p.: 131 °C) was obtained.

Data for 15e: ^{1}H NMR (C_6D_6): $\delta = 7.00$ (m, 2H) and 6.87 (dd, 1H) (3′-, 4′-, 5′-H), 4.28 (dd, $J = 2.3$ Hz, 1H; 9-H), 4.24 (dd, $J = 2.3$ Hz, 1H; 8-H), 4.15 (s, 1H; 12-H), 3.66 and 3.57 (m, 1H each; diastereotopic 10-OCH_2), 3.61 (br s, 4H; CH_2OCH_2), 3.42 and 3.38 (m, 2H; diastereotopic 11-OCH_2), 2.80 and 2.60 (br s, 2H each; NCH_2), 2.21 (dd, $J = 4.8$, 9.2 Hz, 1H; 6-H), 2.60 (m, 1H), 1.62 (m, 4H), 1.48 (m, 1H), 1.24 (m, 1H), and 0.98 (m, 1H) (2-H_2 to 5-H_2), 1.07 and 1.06 (t, 3H each; OCH_2CH_3); ^{13}C NMR (C_6D_6): $\delta = 166.4$ (C_q; C10), 163.0 (C_q; C12), 147.0 (C_q; C2′), 128.6, 126.4, and 124.0 (CH each; C3′-, C4′-, C5′), 97.9 (CH; 9-H), 93.0 (CH; C12), 73.1 (C_q; C7), 67.9 (dynamically broadened CH_2OCH_2), 65.0 (10-OCH_2), 62.6 (11-OCH_2), 55.8 (CH; C6), 51.0 (C_q; C1), 47.8 (dynamically broadened 2NCH_2), 41.9 (CH; C8), 26.8 (CH_2; C5), 24.9 (CH_2; C4), 24.1 (CH_2; C2), 23.2 (CH_2; C3), 14.3 (10-, 11-OCH_2CH_3); MS (70 eV): *m*/*z* (%): 415 (10) $[M]^+$, 386 (100) $[M - C_2H_5]^+$; elemental analysis calcd (%) for $C_{24}H_{33}NO_3S$ (415.6): C 69.36, H 8.00, N 3.37; found: C 69.25, H 8.23, N 3.31.

Data for 16e: ^{1}H NMR (C_6D_6): $\delta = 6.87$ and 6.65 (dd, 1H each; 3′-, 5′-H), 6.71 (m, 1H; 4′-H), 4.87 (s, 1H; 12-H), 3.59 (m, 2H; diastereotopic 11-OCH_2), 3.52 (dd, $J = 7.0$, 9.9 Hz, 1H; 8-H), 3.45 (br, 4H; sCH_2OCH_2), 2.82 (dd, $J = 9.8$, 16.6 Hz, 1H) and 2.62 (dd, $J = 6.8$, 16.7, 1H) (9-H_2), 2.62 and 2.20 (br s, 2H each; NCH_2), 1.87 (dd, $J = 4.3$, 9.6 Hz, 1H; 6-H), 2.38 (m, 1H), 1.83 (m, 1H), 1.58 (m, 4H), 1.21 (m, 1H), and 0.95 (m, 1H) (2-H_2 to 5-H_2), 1.04 (t, 3H; 11-OCH_2CH_3); ^{13}C NMR (C_6D_6): $\delta = 205.4$ (C_q; C10), 161.0 (C_q; C12), 146.9 (C_q; C2′), 126.1, 125.8, and 123.7 (CH; C3′, C4′, C5′), 96.7 (CH; C11), 72.9 (C_q; C7), 68.4 and 67.4 (dynamically broadened CH_2OCH_2), 65.5 (11-OCH_2), 61.6 (C_q; C1), 54.2 (CH; C6), 49.0 and 45.3 (dynamically broadened NCH_2), 47.3 (CH; C8), 44.0 (CH_2; C9), 25.5 (CH_2; C5), 24.4 (CH_2; C4), 23.0 (CH_2; C2), 22.5 (CH_2; C3), 14.3 (11-OCH_2CH_3); IR (KBr): $\tilde{\nu} = 1709.1$ (100), 1630.1 cm^{-1} (30); MS (70 eV): *m*/*z* (%): 387 (10) $[M]^+$, 248 (100); elemental analysis calcd (%) for $C_{22}H_{29}NO_3S$ (387.5): C 68.18, H 7.54, N 3.61; found: C 68.42, H 7.63, N 3.31.

(1*R*,6*S*,7*R*,8*S*)-10,11-Diethoxy-7-[(2*S*)-2-(methoxymethyl)pyrrolidino]-8-phenyltricyclo[5.3.2.0^{1,6}]dodeca-9,11-diene (15f): Reaction of compound

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(3*E*)-**5d** (150 mg, 0.25 mmol), (3*E*)-**14a** (121 mg, 0.25 mmol), and pyridine (20 mg, 0.25 mmol) in [D_6]benzene (1 mL) at 60 °C for 2 h and fast chromatography as described above gave yellow pentacarbonyl(pyridine)-tungsten and the cycloadduct **15f** (61 mg, 56 %, $R_f = 0.7$ in diethyl ether/dichloromethane/*n*-pentane 1:1:4, colorless crystals from dichloromethane/diethyl ether, m.p.: 97 °C). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.16$ (m, 5H; C_6H_5), 4.21 (d, $J = 2.2$ Hz, 1H; 9-H), 4.18 (d, $J = 2.2$ Hz, 1H; 8-H), 4.02 (s, 1H; 12-H), 3.85 (m, 2H; diastereotopic 10-OCH_2), 3.67 and 3.61 (m, 1H each; diastereotopic 11-OCH_2), 3.35 and 2.70 (m, 1H each; diastereotopic CH_3OCH_2), 3.18 (dd, $J = 2.6$, 9.1 Hz, 1H) and 2.72 (dd, $J = 2.4$, 9.4 Hz, 1H) (diastereotopic NCH_2), 3.16 (s, 3H; MeO), 2.34 (m, 1H; NCH), 2.10 (dd, $J = 4.9$, 11.1 Hz, 1H; 6-H), 2.19 and 1.26 (m, 1H each; 2-H_2), 1.72 and 1.60 (m, 2H each; 3′-H_2, 4′-H_2), 1.59 and 1.08 (m, 1H each; 3-H_2), 1.47 and 1.30 (m, 1H each; 5-H_2), 1.63 and 1.06 (m, 1H each; 4-H_2), 1.35 and 1.27 (t, 3H each; OCH_2CH_3); ^{13}C NMR (400 Hz, $CDCl_3$): $\delta = 164.4$ (C_q; C10), 162.1 (C_q; C11), 142.3 (C_q,; C_{ipso} C_6H_5), 129.1, 127.3; and 126.2 (2:2:1, *o*-, *m*-, *p*-C; C_6H_5), 97.4 (CH; C9), 93.7 (CH; C12), 77.5 (CH_3OCH_2), 70.3 (C_q; C1), 64.8 (10-OCH_2), 62.4 (11-OCH_2), 58.7 (OCH_3), 57.0 (NCH), 55.6 (CH; C6), 50.1 (C_q; C1), 45,2 (NCH_2), 42.6 (CH; C8), 29.0 (CH_2; C3′), 25.4 (CH_2; C5), 24.5 (CH_2; C4), 23.6 and 23.5 (CH_2; C2, C4′), 22.8 (CH_2; C3), 14.4 and 14.5 (OCH_2CH_3); MS (70 eV): *m*/*z* (%): 437 (10) $[M]^+$, 408 (30) $[M - Et]^+$; $[\alpha]_D^{20} = 58°$ (in CH_2Cl_2); elemental analysis calcd (%) for $C_{28}H_{39}NO_3$ (437.6): C 76.85, H 8.92, N 3.20; found: C 76.89, H 9.19, N 3.09.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-164075–164077. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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Received: May 25, 2001 [F3289]