Stereocontrolled Synthesis of Angularly Fused Tricyclic Ring Systems by Means of 1-Metalla-1,3,5-hexatrienes (M = Cr, W)**

He-Ping Wu, Rudolf Aumann,* Roland Fröhlich,[+] and Birgit Wibbeling[a]

Abstract: An efficient pathway for the stereocontrolled synthesis of functionalized, angularly fused tricyclic ring systems from readily available (1-alkynyl)-carbene complexes $[(OC)_5M{=}C(OEt)\text{-}C{\equiv}CR]$ (M = Cr, W; R = Ph, *c*-C_6H_9) is described. The synthesis involves the formation of a 1-metalla-1,3,5-hexatriene from the (1-alkynyl)carbene tungsten complex $[(OC)_5W{=}C(OEt)C{\equiv}C\text{-}c\text{-}C_6H_9]$ and a secondary amine, and its thermally induced π-cyclization to a tetrahydroindene, which undergoes a spontaneous isomerization to another tetrahydroindene. Condensation of these tetrahydroindenes with pyran-2-ylidene complexes derived from (1-alkynyl)carbene complexes $[(OC)_5M{=}C(OEt)C{\equiv}CPh]$ (M = Cr, W) proceeds smoothly giving angularly fused tricyclic ring systems, rearrangement of which may generate spiro(cyclopentane-1,1-indanes) as side products. The synthesis is highly versatile and can be applied to the formation of various ring systems, such as steroid-type ring skeletons.

Keywords: annulation · carbene ligands · cycloaddition · steroids · tungsten

Introduction

New strategies for the synthesis of angularly fused tricyclic systems have gained considerable prominence recently as these frameworks exist in many naturally occurring compounds.[1] We became interested in employing 1-metalla-1,3,5-hexatrienes for the construction of angularly fused tri- and polycyclic ring systems. Earlier, we reported on the application of (1-alkynyl)carbene complexes $[(CO)_5M{=}C(OEt)C{\equiv}CR]$ (M = W, Cr; R = aryl, alkenyl) as stoichiometric reagents in high-yielding transformations of potential use in organic synthesis.[2] Prominent examples involve the formation of cyclopentadienes through the π-cyclization of 1-metalla-1,3,5-hexatrienes,[3, 4] derived from (1-alkynyl)carbene complexes, for example, by addition of enamines[5] or various protic nucleophiles NuH (such as $R(R'CO)CH_2$,[6] R_2NH,[7, 8] R_2PH,[7] RC(=O)OH and ROH,[9, 10] RC(=X)SH (X = O, NH, NR),[11] and RSH[12]).[7, 13] The latter procedure was shown to be well suited to the generation of highly reactive bicyclic cyclopentadienes, such as tetrahydropentalenes[7, 8] or tetrahydroindenes.[8, 9] Additionally, it was found that pyran-2-ylidene complexes, which are generated by condensation of (1-alkynyl)carbene complexes with α-CH acidic carbonyl compounds, undergo a cyclohexadiene annelation to electron-rich alkene groups even under very mild conditions.[14] Keeping these reactions in mind, we investigated the condensation of pyran-2-ylidene complexes with tetrahydroindenes as a means of generating angularly fused tricyclic ring systems.

Results and Discussion

Angularly fused tricyclic ring systems: Reaction of the (1-alkynyl)carbene tungsten complex **1** with a secondary amine **2a–2d** and a pyran-2-ylidene complex **3a** or **3b** affords angularly fused tricyclic ring systems **4** [Eq. (1); for substituents and reaction conditions see Tables 1 and 2].

The reaction pathway (Scheme 1) involves addition of **2** to **1** to give a 1-tungsta-1,3,5-hexatriene **5**, which undergoes π-cyclization to a tetrahydroindene tungsten complex **6**.[4, 7] A tetrahydroindene **8** is obtained from **6** by ligand disengagement with pyridine.[15] Tetrahydroindenes **8** have indeed been trapped by cycloaddition reactions[15] as well as by rearrangements.[8] They are notoriously unstable and readily undergo isomerization to tetrahydroindenes **7** by 1,5-hydrogen migration.[15] It was shown by NMR spectroscopy that, for example,

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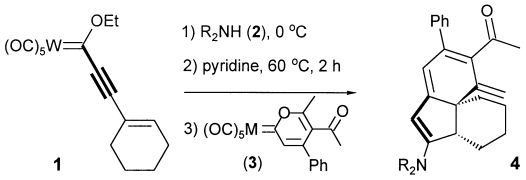
[**] Organic Synthesis via Transition-Metal Complexes, Part 114. For Part 113 see: H.-P. Wu, R. Aumann, R. Fröhlich, B. Wibbeling, and O. Kataeva, *Chem. Eur. J.* **2001**, *7*, 5084.

0947-6539/02/0804-0910 $ 17.50+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 4

the tetrahydroindene **7a** thus obtained reacts smoothly with pyran-2-ylidene tungsten **3a** to give an angularly fused cyclohexadiene annelation product **9a**, even at 20 °C. The reaction involves a [4+2] cycloaddition of the pyranylidene unit to the enol ether unit and the subsequent elimination of $M(CO)_6$ by a retro-Fischer reaction.[14b, 16] The dienophilic character of the enol portion of the 1-amino-3-alkoxybutadiene unit of **7a** is enhanced by π conjugation with an enamine moiety. Compound **9a** was detected as a transient intermediate and characterized by NMR spectroscopy. It was found to eliminate ethanol spontaneously, supposedly to give an intermediate **10a**, from which **4a** is derived by deprotection. Compound **4a** was isolated by chromatography on basic alumina, without decomposition. Thermolysis of **4a** results in smooth rearrangement by a 1,2-carbon migration and aromatization to give the spiro compound **12a**. Compound **4a** is the only product if **7a** is generated and subsequently reacts with **3a** or **3b** at 20 °C; however, **12a** may be obtained as a side product in varying amounts



(1)

Table 1. Compounds **2** and **3**.

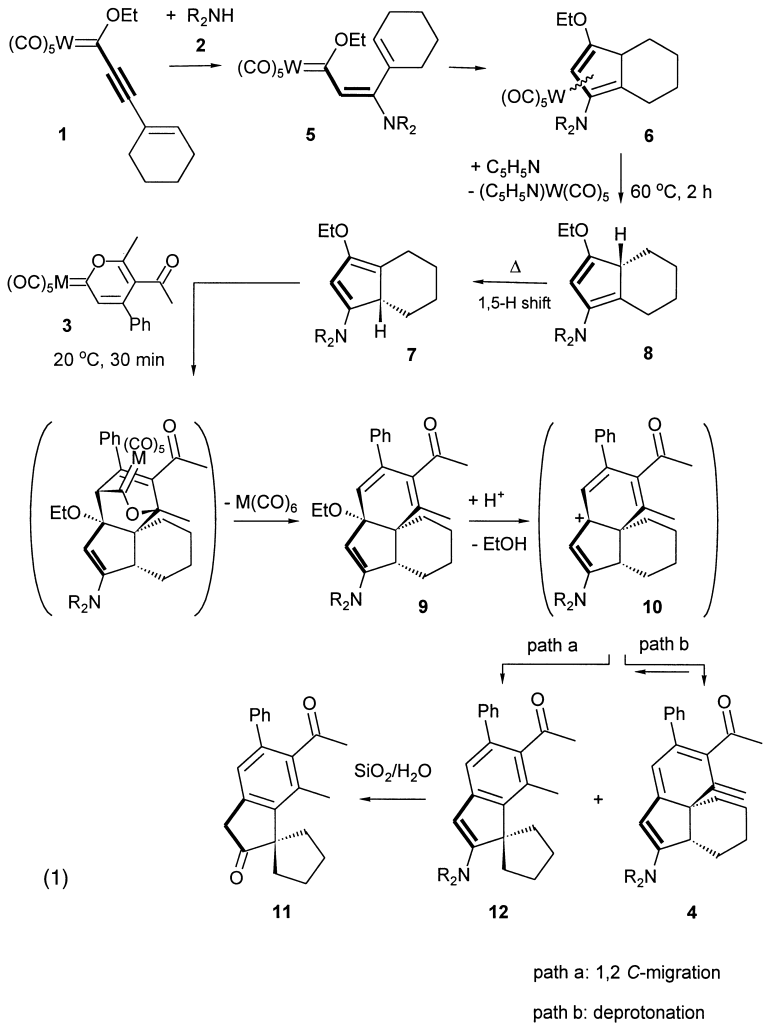
Compound	NR_2	M
2a	NMe_2	–
2b	morpholino	–
2c	piperidino	–
2d	pyrrolidino	–
2e	(2*S*)-MMP[a]	–
3a	–	W
3b	–	Cr

[a] (2*S*)-(−)2-(Methoxymethylene)pyrrolidino.

Table 2. Compounds **4**–**10**, reaction conditions, and yields [see Eq. (1) and Scheme 1].

4–**10**	M	Conditions[a]	NR_2	**4**/**12**/**11**[b]	**11**[c]
a	W	A	NMe_2	54/27/0	35
a	W	B	NMe_2	83/0/0	–
a	Cr	B	NMe_2	75/0/0	–
b	W	A	morpholino	0/63/13	65
b	W	B	morpholino	64/14/7	–
c	W	A	piperidino	28/56/0	–
c	W	B	piperidino	81/0/0	–
d	W	B	pyrrolidino	86/0/0	–
e	W	B	(2*S*)-MMP[d]	84/0/0	–

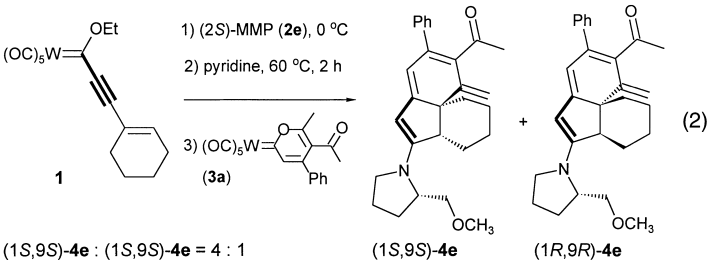
[a] A: compounds **5** were heated with compounds **3** to 65 °C; B: tetrahydroindenes **7** were generated at 65 °C and compounds **3** were added subsequently. [b] Chemical yields [%] of products isolated by chromatography on basic alumina. [c] Isolated by chromatography on silica gel. [d] (2*S*)-MMP = (2*S*)-(2-methoxymethylene)pyrrolidino.



Scheme 1. Reaction pathway leading to compounds **4**.

depending on the amino component and also on the reaction conditions (Scheme 1).

Compound **4e** could be obtained with stereoinduction under the influence of (2*S*)-(2-methoxymethylene)pyrrolidine. The diastereomers (1*S*,9*S*)-**4e** and (1*R*,9*R*)-**4e** were formed in a ratio of 4:1 [Eq. (2)]. This ratio corresponds to the 4:1 diastereomeric ratio of **7e** under equilibrium conditions.[15]



(2)

Compounds **4**, **9**, **11**, and **12** were characterized spectroscopically on the basis of DEPT, COSY, HMQC, and HMBC experiments, and **4a** also by a crystal structure analysis (Figure 1). The bond lengths and bond angles are in line with expectation.

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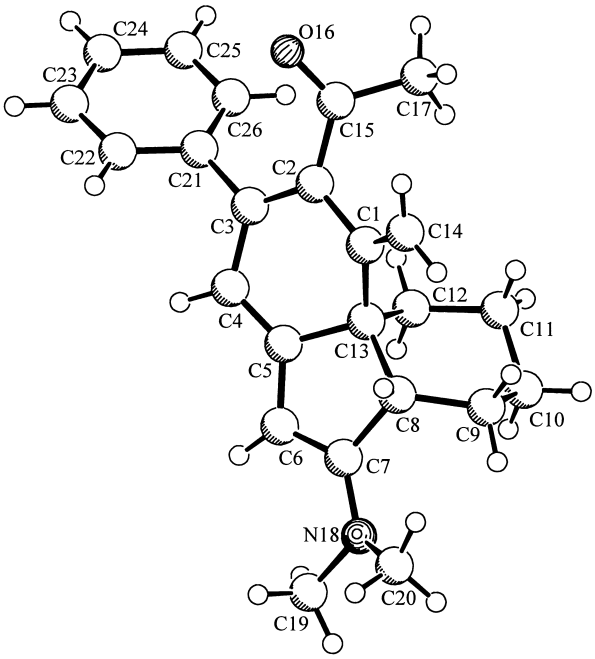
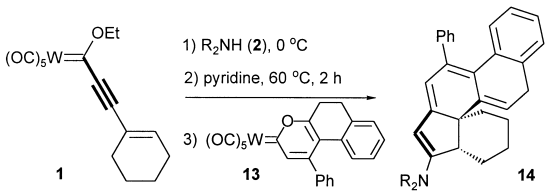


Figure 1. Molecular structure of **4a**. Selected bond lengths [Å] and angles [°]: C1–C2 1.478(3), C1–C13 1.513(3), C2–C3 1.373(3), C3–C4 1.447(3), C4–C5 1.355(3), C5–C6 1.418(3), C5–C13 1.518(3), C6–C7 1.368(3), C7–N18 1.364(3), C7–C8 1.518(3), C8–C9 1.538(3), C8–C13 1.557(3), C9–C10 1.520(3), C10–C11 1.514(4), C11–C12 1.516(3), C12–C13 1.563(3); C2-C1-C13 114.31(18), C3-C2-C1 118.9(2), C2-C3-C4 120.7(2), C5-C4-C3 120.3(2), C4-C5-C6 132.2(2), C4-C5-C13 120.0(2), C6-C5-C13 107.8(2), C7-C6-C5 110.4(2), N18-C7-C6 126.5(2), N18-C7-C8 122.3(2), C6-C7-C8 111.2(2), C7-C8-C9 118.6(2), C7-C8-C13 101.8(2), C9-C8-C13 115.3(2), C10-C9-C8 115.6(2), C11-C10-C9 110.6(2), C10-C11-C12 109.0(2), C11-C12-C13 112.9(2), C1-C13-C5 110.2(2), C1-C13-C8 117.4(2), C5-C13-C8 103.42(2), C1-C13-C12 108.9(2), C5-C13-C12 105.6(2), C8-C13-C12 110.7(2).

Steroid-related angularly fused ring systems: The procedure for generation of angularly fused ring systems requires readily available starting components. The synthesis is highly versatile and can be applied to the formation of various ring systems. For example, a hydrobenzo[14,15]-14β-19-norsteroid[17] skeleton **14** was easily obtained by reaction of 9,10-dihydro-*2H*-benzo[*d*]chromen-2-ylidene complexes **13**[14b] with tetrahydroindenes **7** [Eq. (3) for substituents and reaction conditions, see Table 3]. The reactions at 20 °C of **7b** with



(3)

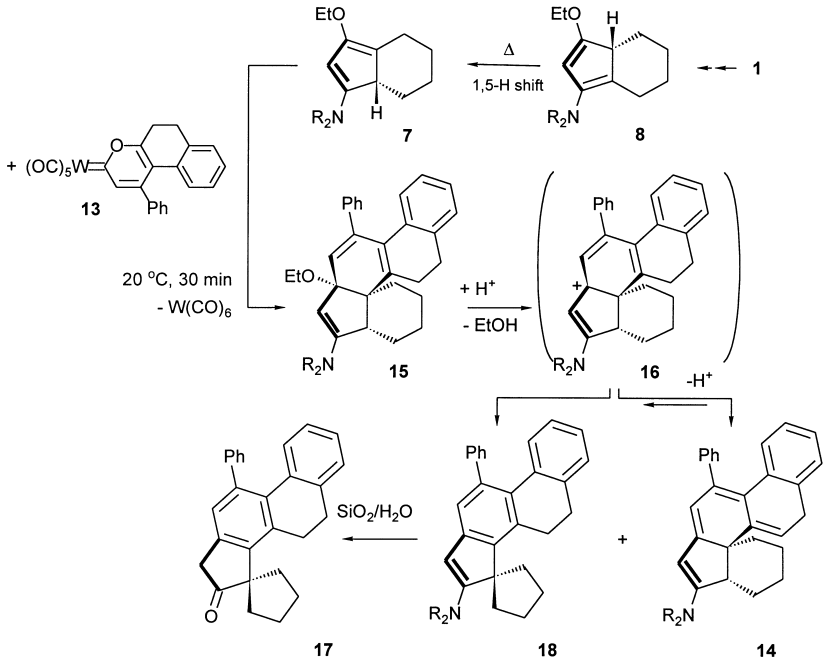
Table 3. Compounds **14**–**18**, conditions and yields [see Eq. (3) and Scheme 2].

14–**18**	NR_2	Conditions[a]	**14/18**	**17**
a	NMe_2	B	[b]	–
b	morpholine	B	76/0[c]	–
b	morpholine	A	21/62[c]	58[d]

[a] A: compounds **5** were heated with compounds **3** to 65 °C; B: tetrahydroindene **7** was formed at 65 °C and reacted subsequently with compounds **3**. [b] A 1:1 ratio of **14a** and [W(pyridine)(CO)$_5$] was observed in the NMR spectra. [c] Chemical yields [%] of products isolated by chromatography on basic alumina. [d] Isolated by chromatography on silica gel.

13, readily generated from [(OC)$_5$M=C(OEt)C≡CPh] (M = Cr, W) and 2-tetralone, produced **14b**, which could be isolated as crystals because of its poor solubility. Reaction of **5b** with the pyran-2-ylidene complex **13** and pyridine at 65 °C provides a 1:3 mixture of **14b** and **18b**. Attempts to isolate **18b** by chromatography on silica gel resulted in formation of the ketone **17** (Scheme 2).

Compounds **14**, **17**, and **18** were characterized by ^{1}H and ^{13}C NMR spectra on the basis of DEPT, COSY, HMQC, and HMBC experiments. The structure of **17** was confirmed by crystal structure analysis (Figure 2).



Scheme 2. Diastereoselectivity of the formation of **4e** induced by (2*S*)-(2-methoxymethylene)pyrrolidine ((2*S*)-MMP; **2e**).

Conclusion

The reaction of **1** with **2** and **3** provides an efficient entry to the generation of angularly fused tricyclic ring systems **4** from readily available starting components. It has also been applied successfully to the synthesis of, for example, a hydrobenzo[14,15]-14β-19-norsteroid skeleton **14** from **1** and **13**.

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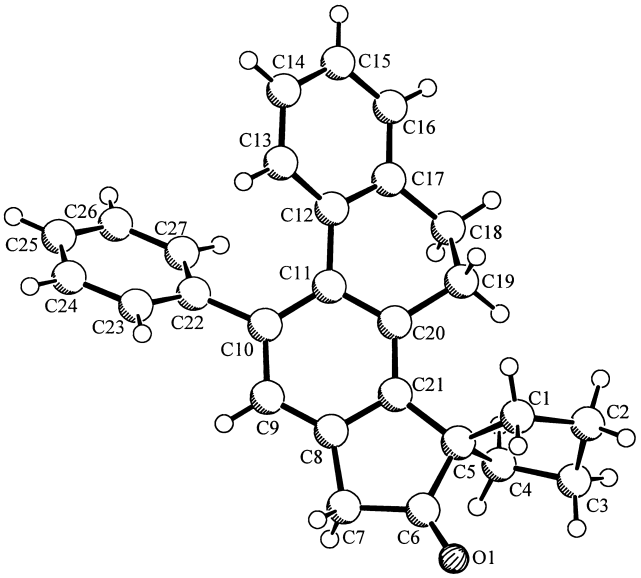
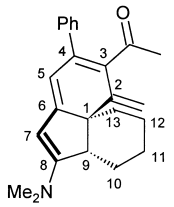


Figure 2. Molecular structure of the steroid-related compound **17**. Selected bond lengths [Å] and angles [°]: C1–C2 1.533(2), C1–C5 1.564(2), C2–C3 1.515(3), C3–C4 1.529(2), C4–C5 1.562(2), C5–C21 1.520(2), C5–C6 1.5352, C6–O1 1.207(2), C6–C7 1.513(2), C7–C8 1.505(2), C8–C9 1.380(2), C8–C21 1.401(2), C9–C10 1.393(2), C10–C11 1.417(2), C11–C20 1.417(2), C11–C12 1.493(2), C12–C17 1.408(2), C17–C18 1.506(2), C18–C19 1.530(2), C19–C20 1.513(2), C20–C21 1.395(2); C2-C1-C5 106.3(1), C3-C2-C1 104.7(1), C2-C3-C4 103.2(1), C3-C4-C5 104.3(1), C21-C5-C6 102.2(1), C21-C5-C4 114.7(1), C6-C5-C4 106.3(1), C21-C5-C1 117.8(1), C6-C5-C1 111.0(1), C4-C5-C1 104.5(1), O1-C6-C7 124.8(1), O1-C6-C5, 125.1(1), C7-C6-C5 110.1(1), C8-C7-C6 103.4(1), C9-C8-C21 120.6(1), C9-C8-C7 128.1(1), C21-C8-C7 111.3(1), C8-C9-C10 120.7(1), C9-C10-C11 119.5(1), C10-C11-C20 119.4(1), C10-C11-C12 123.4(1), C20-C11-C12 117.3(1), C17-C12-C11 118.5(1), C12-C17-C18 117.9(1), C17-C18-C19 109.4(1), C20-C19-C18 109.8(1), C21-C20-C11 119.5(1). C21-C20-C19 122.6(1), C11-C20-C19 117.9(1), C20-C21-C8 120.0(1), C20-C21-C5 128.8(1), C8-C21-C5 111.2(1).

Experimental Section

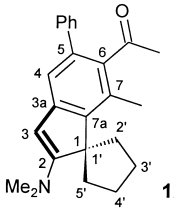
All operations were carried out under an argon atmosphere. All solvents were dried and distilled before use. All ^{1}H and ^{13}C NMR spectra were routinely recorded on Bruker ARX300 and AM360 instruments. COSY, HMQC, HMBC, and NOE experiments were performed on Varian 400 or 600 Hz instruments. IR spectra 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 with iodine. R_f values refer to TLC tests. Pentacarbonyl(3-cyclohexenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1**) was prepared according to reference [7]. Pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (**3a**), -chromium (**3b**), and pentacarbonyl(4-phenyl-9,10-dihydro-2*H*-benzo[*d*]chromen-2-ylidene)tungsten (**13**) were prepared according to reference [16].

3-Acetyl-8-dimethylamino-2-methylene-4-phenyltricyclo[7.4.0.0^{1,6}]deca-3,5,7-triene (4a), 3-acetyl-8-dimethylamino-6-ethoxy-2-methyl-4-phenyltricyclo[7.4.0.0^{1,6}]deca-2,4,7-triene (9a), 6-acetyl-2-dimethylamino-7-methyl-5-phenylspiro(cyclopentane-1,1-indane) (12a), and 6-acetyl-7-methyl-5-phenylspiro[cyclopentane-1,1-indan]-2-one (11): Dimethylamine (**2a**) (23 mg, 0.50 mmol) in toluene (1 mL) at 0 °C [corresponding to 1/10 of a solution of dimethylamine (230 mg) in toluene (10 mL)] was added dropwise to **1** (243 mg, 0.50 mmol) in toluene (1 mL) in a 2 mL screwtop vessel. The point of equivalence was indicated by a color change from brown to yellow. Pyridine (40 mg, 0.50 mmol) was added, and the solution was stirred at 65 °C for 2 h to give the tetrahydroindene derivative **7a**. Addition of **3a** (268 mg, 0.50 mmol) at 20 °C led to precipitation of most of the [W(CO)$_6$], which was removed after 30 min by centrifugation. ^{1}H NMR spectroscopy in [D$_8$]toluene immediately after addition of **3a** to **7a** at 0 °C showed signals of **4a** and **9a** in a ratio of approximately 1:1 as the only detectable products besides [W(pyridine)(CO)$_5$]. Compound **4a** was purified by fast chromatography on basic alumina (column 2 × 15 cm). Elution with *n*-pentane/dichloromethane (3:1) gave yellow [W(pyridine)-(CO)$_5$]. Subsequent elution with diethyl ether/dichloromethane (1:1) afforded **4a** (143 mg, 83 %, m.p. 115 °C). Compound **9a** was not stable under the chromatographic conditions. Reaction of **7a** with **3b** as described above gave a 1:1 mixture of **4a** (total yield approximately 75 %) and pentacarbonyl(pyridine)chromium, but, according to the ^{1}H NMR spectrum, no other products. Reaction of (3*E*)-**5a** (266 mg, 0.50 mmol) with **3a** (268 mg, 0.50 mmol) and pyridine (40 mg, 0.50 mmol) in toluene (2 mL) in a 2 mL screwtop vessel at 65 °C for 2.5 h gave a 2:1 mixture of **4a** and **12a** (140 mg, 81 %, **4a**/**12a** = 2:1) together with pentacarbonyl(pyridine)tungsten. The compounds could be separated by chromatography on alumina (column 2 × 10 cm), but chromatography on silica gel with *n*-pentane/dichloromethane (2:1) gave **11** {55 mg, 35 %, R_f = 0.5 in *n*-pentane/dichloromethane (2:1), m.p. 159 °C} by hydrolysis of **12a**.



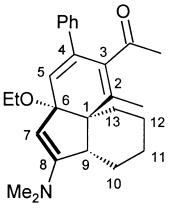
4a

Data for 4a: ^{1}H NMR (400 MHz, C_6D_6): δ = 7.36 and 7.15 (m, 2:3 H; C_6H_5), 5.74 (s, 1 H; 5-H), 5.54 and 5.23 (s, each 1 H; =CH_2), 5.22 (s, 1 H; 7-H), 2.71 (m, 1 H; 9-H), 2.43 (s, 6 H; $N(CH_3)_2$), 1.90 (s, 3 H; $COCH_3$), 1.87 and 1.70 (m, each 1 H), 1.85 and 1.24 (m, each 1 H), 1.48 and 1.18 (m, 2 H), 1.40 and 1.25 (m, each 1 H) (10-CH_2 to 13-CH_2); ^{13}C NMR (400 Hz, C_6D_6): δ = 204.7 (C_q, C=O), 167.0 (C_q, C8), 161.4 (C_q, C6), 148.6, 142.3, 139.6, and 129.2 (C_q, C*i*, C2–C4), 128.7, 128.6, and 127.8 (CH, 2:2:1, C_6H_5), 110.7 (=CH_2), 106.6 (CH, C5), 102.9 (CH, C7), 49.0 (C_q, C1), 47.5 (CH, C9), 40.9 ($N(CH_3)_2$), 31.9 ($COCH_3$), 35.4, 24.3, 22.9, and 18.6 (CH_2, C10–C13); IR (KBr): $\tilde{\nu}$ = 1699.0 cm^{-1} (100) (C=O); MS (70 eV): *m*/*z* (%): 345 (100) $[M]^+$, 302 (95) $[M-43]^+$; elemental analysis calcd (%) for $C_{24}H_{27}NO$ (345.2): C 83.44, H 7.88, N 4.05; found: C 82.96, H 7.72, N 3.79; X-ray crystal structure analysis: formula $C_{24}H_{27}NO$, M = 345.47, red crystals 0.25 × 0.20 × 0.05 mm, a = 13.326(4), b = 8.634(2), c = 16.719(4) Å, β = 98.59(2)°, V = 1902.1(9) Å^3, ρ_{calcd} = 1.206 g cm^{-3}, μ = 5.58 cm^{-1}, empirical absorption correction from ψ scan data (0.873 ≤ T ≤ 0.973), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223 K, $\omega/2\theta$ scans, 4013 reflections collected ($\pm h$, $+k$, $+l$), [(sinθ)/λ] = 0.62 Å^{-1}, 3878 independent (R_{int} = 0.035) and 2507 observed reflections [$I \geq 2\sigma(I)$], 239 refined parameters, R = 0.053, wR^2 = 0.146, max/min residual electron density 0.28/−0.24 e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.[18]



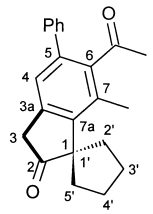
12a

Data for 12a: ^{1}H NMR (C_6D_6): δ = 7.45 and 7.12 (m, 2:3 H; C_6H_5), 6.92 (s, 1 H; 4-H), 5.26 (s, 1 H; 3-H), 2.49 (s, 6 H; $N(CH_3)_2$), 2.32 (s, 3 H; 7-CH_3), 2.28–1.85 (m, 8 H; 2′-CH_2 to 5′-CH_2), 1.87 (s, 3 H; $COCH_3$); ^{13}C NMR (C_6D_6): δ = 207.0 (C_q, C=O), 167.4 (C_q, C2), 148.5, 145.7, 142.6, 138.2, 136.7, and 127.3 (C_q; C*i*, C3a, C7a, C5–C7), 129.4, 128.6, and 127.8 (CH, 2:2:1, C_6H_5), 117.1 (CH, C4), 100.4 (CH, C3), 60.9 (C_q, C1), 41.8 ($N(CH_3)_2$), 32.9 ($COCH_3$), 34.4 and 28.1 (2 CH_2, C2′–C5′), 16.1 (7-CH_3).



9a

Data for 9a: ^{1}H NMR (400 MHz, C_6D_6): δ = 7.32 and 7.10 (m, 2:3 H; C_6H_5), 5.97 (s, 1 H; 5-H), 4.16 (s, 1 H; 7-H), 3.58 and 3.40 (m, each 1 H; diastereotopic 6-OCH_2), 2.75 (dd, 1 H; 9-H), 2.45 (s, 6 H; $N(CH_3)_2$), 1.90 (s, 3 H; 2-CH_3), 2.04 and 1.54 (m, each 1 H), 2.03 and 1.22 (m, each 1 H), 1.95 (m, 2 H), 1.88 and 1.70 (m, each 1 H) (10-CH_2 to 13-CH_2), 1.60 (s, 3 H; $COCH_3$), 1.14 (t, 3 H; OCH_2CH_3), 0.87 (t, 3 H; OCH_2CH_3); ^{13}C NMR (400 MHz, C_6D_6): δ = 205.3 (C_q, C=O), 162.1 (C_q, C8), 144.1, 142.1, 135.4, and 132.9 (C_q, C*i*, C2–C4), 128.5, 127.8, and 127.3 (CH, 2:2:1, C_6H_5), 128.5 (CH, C5), 92.2 (CH, C7), 89.8 (C_q, C6), 56.4 (6-OCH_2), 52.8 (C_q, C1), 45.7 (CH, C9), 39.7 ($N(CH_3)_2$), 31.1 ($COCH_3$), 30.0, 26.5, 25.2, and 24.9 (CH_2, C10–C13), 16.1 (OCH_2CH_3), 15.6 (2-CH_3).



11

Data for 11: ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.36$, 7.16, and 7.11 (m, 2:2:1 H; C_6H_5), 6.75 (s, 1 H; 4-H), 3.20 (s, 2 H; 3-CH_2), 2.14 (s, 3 H; 7-CH_3), 1.95 and 1.67 (m, each 4 H; 2′-CH_2 to 5′-CH_2), 1.79 (s, 3 H; $COCH_3$); ^{13}C NMR (C_6D_6): $\delta = 218.7$ (C_q, C2), 206.1 (C_q, *C*OCH_3); 144.8, 143.0, 140.9, 137.5, and 129.7 (C_q, 1:1:1:2:1, C*i*, C3a, C7a, C5 – C7); 129.7, 128.8, and 127.8 (CH, 2:2:1, C_6H_5), 123.8 (CH, C4), 60.6 (C_q, C1), 41.6 (CH_2, C3), 32.2 (CO*C*H_3), 36.9 and 27.5 (2 CH_2, C2′ – C5′), 15.7 (7-CH_3); IR (KBr): $\tilde{\nu} = 1741.2$, 1694.9 cm^{-1} (C=O); MS (70 eV): *m/z* (%): 318 (80) $[M]^+$, 303 (100) $[M-15]^+$; elemental analysis calcd (%) for $C_{22}H_{22}O_2$ (318.4): C 82.99, H 6.96; found: C 82.72, H 6.84.

3-Acetyl-2-methylene-4-phenyl-8-morpholinotricyclo[7.4.0.0^{1,6}]deca-3,5,7-triene (4b) and 6-acetyl-7-methyl-5-phenyl-2-morpholinospiro(cyclopentane-1,1-indane) (12b): Reaction of **1a** (243 mg, 0.50 mmol) with morpholine (**2b**) (44 mg, 0.50 mmol) as described above gave **7b**, which reacted with **3a** (268 mg, 0.50 mmol) to give a mixture (approximately 3:1:4) of **4b**, **12b**, and [W(pyridine)(CO)$_5$] according to an ^{1}H NMR spectrum. Fast chromatography on basic alumina (column 2 × 15 cm) with *n*-pentane/dichloromethane (4:1) gave a yellow band of [W(pyridine)(CO)$_5$], a fraction containing **12b** and **11** (38 mg, 21 %, **12b**/**11** = 2:1), and finally with diethyl ether/dichloromethane (1:1) a fraction with **4b** (124 mg, 64 %, m.p. 128 °C). A 3:1:4 mixture of **4b**, **12b**, and [W(pyridine)(CO)$_5$] in [D$_6$]benzene at 65 °C for 30 h was transformed into a 1:10:10 mixture of **4b**, **12b**, and [W(pyridine)(CO)$_5$] as shown by ^{1}H NMR spectra. Compound (3*E*)-**5b** (286 mg, 0.5 mmol), pyran-2-ylidene complex **3a** (268 mg, 0.50 mmol), and pyridine (40 mg, 0.50 mmol) reacted as described above to give a mixture (approximately 1:20:20) of **4b**, **12b**, and [W(pyridine)(CO)$_5$] as indicated by ^{1}H NMR spectra. Chromatography on basic alumina (column 2 × 15 cm) yielded a mixture of **12b** and **11** (142 mg, 76 %, **12b**/**11** = 5:1), from which **11** (103 mg, 65 %) could be isolated by chromatography on silica gel (column 2 × 15 cm) with *n*-pentane/dichloromethane (2:1).

Data for 4b: ^{1}H NMR (C_6D_6): $\delta = 7.44$ and 7.10 (m, 2:3 H; C_6H_5), 5.93 (s, 1 H; 5-H), 5.71 and 5.29 (br s, each 1 H; =CH_2), 5.25 (s, 1 H; 7-H), 3.41 (m, 4 H; 2 OCH_2), 2.66 (d d, $J = 3.6$, 5.8 Hz, 1 H; 9-H), 2.40 (m, 4 H; 2 NCH_2), 1.94 (s, 3 H; $COCH_3$); 1.90 (m, 1 H), 1.80 (m, 1 H), 1.60 (m, 2 H), 1.38 (m, 1 H), 1.20 (m, 3 H) (10-CH_2 to 13-CH_2); ^{13}C NMR (C_6D_6): $\delta = 204.5$ (C_q, C=O), 165.3 (C_q, C8), 159.5 (C_q, C6); 148.2, 141.9, 138.2, and 129.5 (C_q, C*i*, C2 – C4), 128.7 and 127.8 (CH, 4:1, C_6H_5), 112.0 (=CH_2), 109.2 (CH, C5), 105.1 (CH, C7), 66.2 (2 OCH_2), 50.0 (2 NCH_2), 48.4 (C_q, C1), 46.8 (CH, C9), 31.9 (CO*C*H_3); 34.8, 24.3, 23.4, and 18.5 (CH_2, C10 – C13); IR (KBr): $\tilde{\nu} = 1698.6$ cm^{-1} (C=O); MS (70 eV): *m/z* (%): 387 (100) $[M]^+$; elemental analysis calcd (%) for $C_{26}H_{29}NO_2$ (387.2): C 80.57, H 7.55, N 3.62; found: C 80.40, H 7.45, N 3.47.

Data for 12b: ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.45$ and 7.14 (m, 2:3 H; C_6H_5), 6.99 (s, 1 H; 4-H), 5.47 (s, 1 H; 3-H), 3.52 (m, 4 H; 2 OCH_2), 2.74 (m, 4 H; 2 NCH_2), 2.33 (s, 3 H; 7-CH_3), 2.22 and 1.96 (m, each 2 H), 1.95 and 1.80 (m, each 2 H; 2′-CH_2 to 5′-CH_2), 1.86 (s, 3 H; $COCH_3$); ^{13}C NMR (400 MHz, C_6D_6): $\delta = 207.0$ (C_q, C=O), 168.3 (C_q, C2), 148.3, 144.5, 142.2, 138.6, 138.0, and 127.1 (C_q, C*i*, C3a, C7a, C5 – C7); 129.7, 128.7, and 127.5 (CH, 2:2:1, C_6H_5), 118.3 (CH, C4), 105.3 (CH, C3), 68.7 (2 OCH_2), 61.1 (C_q, C1), 51.0 (2 NCH_2), 32.8 (CO*C*H_3), 34.3 and 27.9 (2 CH_2, C2′ – C5′), 16.0 (7-CH_3).

3-Acetyl-2-methylene-4-phenyl-8-piperidinotricyclo[7.4.0.0^{1,6}]deca-3,5,7-triene (4c) and 6-acetyl-7-methyl-5-phenyl-2-piperidinospiro(cyclopentane-1,1-indane) (12c): Tetrahydroindene **7c**, which was prepared as described above from **1a** (243 mg, 0.50 mmol) and piperidine (**2c**) (42 mg, 0.50 mmol), was treated with **3a** (268 mg, 0.50 mmol) to give a 1:1 mixture of **4c** with [W(pyridine)(CO)$_5$] according to ^{1}H NMR spectra. Fast chromatography on alumina (column 2 × 15 cm) with *n*-pentane/dichloromethane (4:1) gave [W(pyridine)(CO)$_5$], then with diethyl ether/dichloromethane (1:1) afforded **4c** (156 mg, 81 %, m.p. 151 °C). Reaction of (3*E*)-**5c** (285 mg, 0.50 mmol) with **3a** (268 mg, 0.50 mmol) and pyridine (40 mg, 0.50 mmol) as described above gave a 1:2:3 mixture of **4c**, **12c**, and [W(pyridine)(CO)$_5$] according to ^{1}H NMR spectra. Fast chromatography on basic alumina (column 2 × 10 cm) with *n*-pentane/dichloromethane/diethyl ether (1:1:1) gave a mixture of **4c** and **12c** (156 mg, 83 %, **4c**/**12c** = 1:2).

Data for 4c: ^{1}H NMR (C_6D_6): $\delta = 7.39$ and 7.11 (m, 2:3 H; C_6H_5), 5.83 (s, 1 H; 5-H), 5.61 and 5.32 (s, each 1 H; =CH_2), 5.28 (s, 1 H; 7-H), 2.70 (m, 1 H; 9-H), 2.80 and 2.63 (m, each 2 H; 2 NCH_2), 1.91 (s, 3 H; $COCH_3$); 1.85 (m, 2 H), 1.67 (m, 1 H), 1.51 (m, 2 H), 1.32 (m, 9 H) (10-CH_2 to 13-CH_2, 3 CH_2 piperidino); ^{13}C NMR (C_6D_6): $\delta = 204.6$ (C_q, C=O), 166.5 (C_q, C8), 160.9 (C_q, C6), 148.5, 142.2, 138.9, and 129.6 (C_q, C*i*, C2 – C4), 128.9, 128.6, and 127.8 (CH, 2:2:1, C_6H_5), 111.4 (=CH_2), 107.6 (CH, C5), 104.0 (CH, C7), 50.5 (2 NCH_2), 48.5 (C_q, C1), 47.2 (CH, C9), 31.9 (CO*C*H_3), 35.0, 24.5, 23.4, and 18.7 (CH_2, C10 – C13), 25.6 and 24.3 (2:1 CH_2, 3 CH_2 piperidino); IR (KBr): $\tilde{\nu} = 1699.0$ (C=O), 1699.3 cm^{-1} (C=O); MS (70 eV): *m/z* (%): 385.2 (100) $[M]^+$; elemental analysis calcd (%) for $C_{27}H_{31}NO$ (385.2): C 84.10, H 8.11, N 3.63; found: C 83.92, H 7.99, N 3.40.

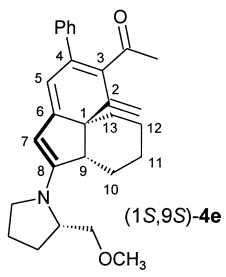
Data for 12c: ^{1}H NMR (C_6D_6): $\delta = 7.44$ and 7.11 (m, 2:3 H; C_6H_5), 6.95 (s, 1 H; 4-H), 5.51 (s, 1 H; 3-H), 2.85 (m, 4 H; 2 NCH_2), 2.21 (s, 3 H; 7-CH_3), 2.21 and 1.95 (m, each 2 H), 1.94 and 1.81 (m, each 2 H) (2′-CH_2 to 5′-CH_2), 1.32 (m, 6 H; 3 CH_2 piperidino), 1.85 (s, 3 H; $COCH_3$); ^{13}C NMR (C_6D_6): $\delta =$ 207.0 (C_q, C=O), 168.9 (C_q, C2), 148.2, 145.2, 142.4, 137.9, and 126.9 (C_q, 1:1:1:2:1, C*i*, C3a, C7a, C5 – C7), 129.5, 128.6, and 127.4 (CH, 2:2:1, C_6H_5), 117.8 (CH, C4), 103.9 (CH, C3), 61.3 (C_q, C1), 51.2 (2 NCH_2), 32.8 (CO*C*H_3), 34.7 and 28.0 (2 CH_2, C2′ – C5′), 26.1 and 24.4 (2:1 CH_2 piperidino), 16.0 (7-CH_3).

3-Acetyl-2-methylene-4-phenyl-8-pyrrolidinotricyclo[7.4.0.0^{1,6}]deca-3,5,7-triene (4d) and 6-acetyl-7-methyl-5-phenyl-2-pyrrolidinospiro(cyclopentane-1,1-indane) (12d): Tetrahydroindene **7d**, which was prepared as described above from **1a** (243 mg, 0.50 mmol) and pyrrolidine (**2d**) (36 mg, 0.50 mmol), subsequently reacted with **3a** (268 mg, 0.50 mmol) to give a mixture (approximately 1:1) of **4d** with [W(pyridine)(CO)$_5$] as indicated by ^{1}H NMR spectra. Fast chromatography on basic alumina (column 2 × 15 cm) gave [W(pyridine)(CO)$_5$] and **4d** (159 mg, 86 %, m.p. 150 °C).

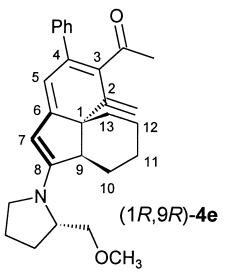
Data for 4d: ^{1}H NMR (C_6D_6): $\delta = 7.48$ and 7.10 (m, 2:3 H; C_6H_5), 5.84 (s, 1 H; 5-H), 5.82 and 5.41 (s, each 1 H; =CH_2), 5.11 (s, 1 H; 7-H), 2.76 (m, 1 H; 9-H), 2.78 (m, 4 H; 2 NCH_2), 1.98 (s, 3 H; $COCH_3$), 2.07 (m, 1 H), 1.87 (m, 1 H), 1.71 (m, 2 H), 1.48 (m, 2 H), 1.37 (m, 3 H) 1.22 (m, 3 H) (10-CH_2 to 13-CH_2, 2 CH_2 pyrrolidino); ^{13}C NMR (C_6D_6): $\delta = 204.0$ (C_q, C=O), 163.5 (C_q, C8), 162.0 (C_q, C6); 148.8, 142.8, 140.7, and 129.3 (C_q, C*i*, C2 – C4), 128.8, 128.5, and 128.3 (CH, 2:2:1, C_6H_5), 109.8 (=CH_2), 105.2 (CH, C5), 99.4 (CH, C7), 49.8 (2 NCH_2), 49.2 (C_q, C1), 48.0 (CH, C9), 32.1 (CO*C*H_3), 35.3, 24.1, 22.6, and 18.9 (CH_2, C10 – C13), 25.6 (2 CH_2 pyrrolidino); IR (KBr): $\tilde{\nu} = 1700.4$ cm^{-1}; MS (70 eV): *m/z* (%): 371 (100) $[M]^+$; elemental analysis calcd (%) for $C_{26}H_{29}NO$ (371.2): C 84.06, H 7.87, N 3.77; found: C 84.24, H 7.62, N 3.51.

3-Acetyl-2-methylene-4-phenyl-8-[(2*S*)-2-(methoxymethyl)pyrrolidino]tricyclo[7.4.0.0^{1,6}]deca-3,5,7-triene ((1*S*,9*S*)-4e and (1*R*,9*R*)-4e): Tetrahydroindene **7e**, prepared as described above from **1a** (243 mg, 0.50 mmol) and **2e** (58 mg, 0.50 mmol), subsequently reacted with complex **3a** (268 mg, 0.50 mmol) to give a mixture (approximately 4:1:5) of (1*S*,9*S*)-**4e**, (1*R*,9*R*)-**4e**, and [W(pyridine)(CO)$_5$] as indicated by ^{1}H NMR spectra. Fast chromatography on basic alumina (column 2 × 15 cm) gave [W(pyridine)-(CO)$_5$], (1*S*,9*S*)-**4e**, and (1*R*,9*R*)-**4e** (174 mg, 84 %).

Data for (1S,9S)-4e {(1R,9R)-4e}: ^{1}H NMR (C_6D_6): $\delta = 7.46$ and 7.12 {7.45 and 7.12} (m, 2:3 H; *o*-, *m*-, *p*-H C_6H_5), 5.77 {5.81} (s, 1 H , 5-H), 5.76 and 5.38 {5.76 and 5.38} (s, each 1 H; =CH_2), 5.26 {5.19} (s, 1 H; 7-H), 3.58 {3.74} (m, 1 H; NCH), 3.29 and 3.12 {3.29 and 3.13} (m, each 1 H; OCH_2), 3.07 {3.07} (m, 2 H; NCH_2), 3.08 {3.05} (s, 1 H; OCH_3), 2.81 {2.81} (b, 1 H; 9-H), 2.97 {2.97} (m, 1 H), 1.95 {1.95} (m, 1 H), 1.82 – 1.62 {1.82 – 1.62} (m, 1 H), 1.55 – 1.22 {1.55 – 1.22} (m, 7 H) (10-CH_2 to 13-CH_2, 2 CH_2 pyrrolidino), 1.95 {1.96} (s, 3 H; $COCH_3$); ^{13}C NMR (C_6D_6): $\delta = 204.1$ {203.9} (C_q, C=O), 163.1 {162.0} (C_q, C8), 161.8 {161.6} (C_q, C6), 148.8 {148.8}, 142.6 {142.8}, 140.2 and 129.1 {140.8 and 129.3} (C_q, Ci, C2 – C4); 128.8, 128.5, and 127.8 {128.8, 128.5, and 127.8} (2:2:1, *o*-, *m*-, *p*-C C_6H_5), 110.1 {109.2} (=CH_2), 105.9



(1*S*,9*S*)-**4e**



(1*R*,9*R*)-**4e**

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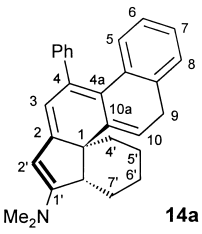
{105.5} (CH, C5), 101.1 {100.0} (CH, C7), 73.1 {72.6} (OCH_2), 59.9 {60.6} (NCH), 58.9 {58.8} (OCH_3), 50.8 {49.8} (NCH_2), 49.0 {49.0} (C_q, C1), 48.7 {47.9} (CH, C9), 32.2 {32.0} ($COCH_3$); 35.5, 24.2, 22.6, and 18.8 {35.2, 23.2, 22.5, and 19.2} (CH_2, C10–C13), 29.3 and 24.7 {28.7 and 24.3} ($2CH_2$ pyrrolidino); IR (KBr): $\tilde{\nu} = 1699.8\ cm^{-1}$ (C=O); MS (70 eV): *m/z* (%): 415 (100) $[M]^+$; elemental analysis calcd (%) for $C_{28}H_{33}NO_2$ (415.6): C 80.93, H 8.00, N 3.37; found: C 80.74, H 7.92, N 3.56.

4-Phenyl-1,2(3,3a)-(1-dimethylamino-3a,4,5,6,7,7a-hexahydro-3*H*-indeno)-phenanthrene (14a): Tetrahydroindene **7a** (0.50 mmol), prepared as described above, reacted with **13** (291 mg, 0.50 mmol) at 20 °C for 30 min to give a 1:1 mixture of **14a** with [W(pyridine)$(CO)_5$] as indicated by ^{1}H NMR spectra. Fast chromatography on basic alumina (column 2 × 15 cm) gave **14a**.

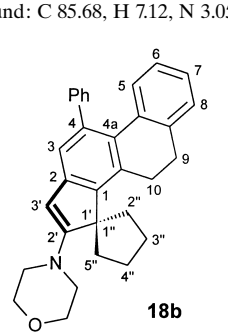
Data for 14a: ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.40$ and 7.10 (m, 2:3H; C_6H_5), 7.09 (m, 2H; 5-, 8-H), 6.89 and 6.72 (t, each 1H; 6-, 7-H), 6.05 (m, 1H; 10-H), 5.88 (s, 1H; 3-H), 5.25 (s, 1H; 2′-H), 3.50 (m, 2H; 9-CH_2), 2.84 (d, 1H; 7′a-H), 2.39 (m, 6H; $N(CH_3)_2$), 2.00 (m, 1H), 1.71 (m, 1H), 1.45 (m, 2H), 1.15 (m, 4H) (4′-CH_2 to 7′-CH_2); ^{13}C NMR (400 MHz, C_6D_6): $\delta = 165.2$ (C_q, C1′), 158.3 (C_q, C2); 145.4, 144.5, 136.5, 136.0, and 133.8 (C_q, 1:1:1:1:2, C*i*, 4, 4a, 4b, 8a, 10a), 130.0, 128.6, and 127.8 (CH, 2:2:1, C_6H_5), 129.5 and 126.9 (CH, C6, C7), 125.1 and 125.2 (CH, C5, C8), 120.4 (CH, C10), 110.8 (CH, C3), 103.9 (CH, C2′), 48.1 (C_q, C1), 47.4 (CH, C7′a), 41.2 ($N(CH_3)_2$), 33.3 (CH_2, C9), 33.9, 24.4, 23.5, and 19.1 (CH_2, C4′–C7′); MS (70 eV): *m/z* (%): 391 (100) $[M]^+$.



14a

4-Phenyl-1,2(3,3a)-(1-morpholino-3a,4,5,6,7,7a-hexahydro-3*H*-indeno)-phenanthrene (14b), 4-phenyl-1,2(4,5)-spiro[cyclopentane-1,1-(2-morpholino)cyclopentadieno]phenanthrene (18b), and 4-phenyl-1,2(4,5)-spiro[cyclopentane-1,1-(2-oxocyclopenteno)]phenanthrene (17): Tetrahydroindene **7b** (0.50 mmol), prepared as described above, reacted with **13** (291 mg, 0.50 mmol) at 20 °C for 30 min. The solvent was removed, and the residue was washed three times with diethyl ether/*n*-pentane (1:1) (2 mL each time), dissolved in dichloromethane (2 mL), and separated by fast chromatography on basic alumina (column 2 × 15 cm) with dichloromethane/diethyl ether (1:1) to give **14b** (164 mg, 76%, m.p. 194 °C). Reaction of (3*E*)-**5b** (286 mg, 0.50 mmol) with **13** (291 mg, 0.50 mmol) and pyridine (40 mg, 0.50 mmol) at 65 °C for 3 h gave a mixture of **14b** and **18b** (180 mg, 83%, **14b**/**18b** = 1:3), which was separated on silica gel with *n*-pentane/dichloromethane (1:1) to give **17** (105 mg, 58%, m.p. 188 °C).

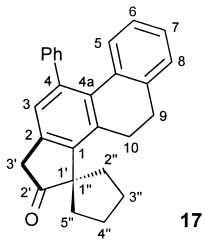
Data for 14b: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.24$ (m, 5H; C_6H_5), 7.11, 6.96, and 6.74 (m, 1:1:2H; 5-H–8-H), 6.18 (t, $J = 4.5$ Hz, 1H; 10-H), 5.77 (s, 1H; 3-H), 5.26 (d, $J = 1.4$ Hz, 1H; 2′-H), 3.78 (m, 4H; 2 OCH_2), 3.54 (d, $J = 5.0$ Hz, 2H; 9-CH_2), 3.14 and 2.87 (m, each 2H; $2NCH_2$), 2.92 (d, $J = 5.9$ Hz, 1H; 7′a-H), 2.06 and 1.84 (m, each 1H), 1.74 and 1.05 (m, each 1H), 1.58 and 1.20 (m, each 1H) and 1.15 (m, 2H) (4′-CH_2 to 7′-CH_2); ^{13}C NMR (400 MHz, C_6D_6): $\delta = 163.8$ (C_q, C1′), 156.8 (C_q, C2), 144.2, 143.5, 135.7, 135.6, 132.6, and 121.0 (C_q; C*i*, 4, 4a, 4b, 8a, 10a), 129.5, 128.2, and 126.5 (CH, 2:2:1, C_6H_5), 129.0 and 127.3 (CH, C6, C7), 125.5 and 124.7 (CH, C5, C8), 121.1 (CH, C10), 111.9 (CH, C3), 105.1 (CH, C2′), 66.4 ($2OCH_2$), 50.0 ($2NCH_2$), 47.1 (C_q, C1), 46.3 (CH, C7′a), 33.0 (CH_2, C9), 32.9, 24.0, 23.3, and 18.8 (CH_2 each, C4′–C7′); MS (70 eV): *m/z* (%): 433 (100) $[M]^+$; elemental analysis calcd (%) for $C_{31}H_{31}NO$ (433.2): C 85.87, H 7.21, N 3.23; found: C 85.68, H 7.12, N 3.05.



18b

Data for 18b: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.24$ (m, 5H; C_6H_5); 7.10, 6.96, and 6.74 (m, 1:1:2H; 5-H–8-H), 7.0 (s, 1H; 3-H), 5.66 (s, 1H; 3′-H), 3.79 (m, 4H; $2OCH_2$), 3.06 (m, 4H; $2NCH_2$), 2.80 (m, 4H; 9-H, 10-CH_2), 2.10 (m, 8H) (2″-CH_2 to 5″-CH_2); ^{13}C NMR (400 MHz, C_6D_6): $\delta = 167.8$ (C_q, C2′), 145.9 (C_q, C2), 142.2, 138.9, 138.7, 134.9, 133.4, and 120.5 (C_q; C*i*, 4, 4a, 4b, 8a, 10a), 129.7, 128.2, and 126.6 (CH, 2:2:1, C_6H_5), 130.2 and 128.4 (CH, C6, C7), 125.3 and 125.1 (CH, C5, C8), 126.2 (CH, C3), 105.7 (CH, C3′), 66.9 ($2OCH_2$), 60.6 (C_q, C1′), 51.0 ($2NCH_2$), 34.8 and 27.7 ($2CH_2$, C2′–C5′), 29.6 and 26.3 (CH_2, C9, C10).

Data for 17: ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.28$, 7.14, and 7.12 (2:2:1H; C_6H_5); 7.10 (m, 2H; C5, C8), 6.93 (s, 1H; 3-H), 6.95 and 6.77 (dt, each 1H; 6-H, 7-H), 3.26 (s, 2H; 3′-H), 2.65 and 2.51 (m, each 2H; 9-H, 10-CH_2), 2.02 and 1.76 (m, each 4H; 2″-CH_2 to 5″-CH_2), ^{13}C NMR (400 MHz, C_6D_6): $\delta = 219.1$ (C_q, C2′), 144.0 (C_q, C2), 143.1, 139.6, 139.2, 136.4, 135.8, 134.6, and 133.7 (C_q, C*i*, C1, C4, C4a, C4b, C8a, C10a), 130.0, 128.7, and 127.3 (CH, 2:2:1, C_6H_5), 126.5 (CH, C3), 60.5 (C_q, C1′), 41.6 (CH_2, C3′), 37.2 and 27.6 ($2CH_2$, C2′–C5′), 29.8 and 26.5 (CH_2, C9, C10); IR (KBr): $\tilde{\nu} = 1741.6\ cm^{-1}$; MS (70 eV): *m/z* (%): 364 (100) $[M]^+$; elemental analysis calcd (%) for $C_{27}H_{24}O$ (364.2): C 88.97, H 6.64; found: C 88.79, H 6.51; X-ray crystal structure analysis: formula $C_{27}H_{24}O$, $M = 364.46$, light yellow crystal $0.15 \times 0.15 \times 0.15$ mm, $a = 8.389(1)$, $b = 12.283(1)$, $c = 18.895(1)$ Å, $\beta = 97.08(1)°$, $V = 1932.1(3)$ Å^3, $\rho_{calcd} = 1.253\ g\,cm^{-3}$, $\mu = 0.74\ cm^{-1}$, empirical absorption correction by *SORTAV* ($0.989 \le T \le 0.989$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 8482 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.68\ Å^{-1}$, 4844 independent ($R_{int} = 0.038$) and 3614 observed reflections [$I \ge 2\sigma(I)$], 253 refined parameters, $R = 0.055$, $wR^2 = 0.120$, max/min residual electron density 0.22/ $-0.19\ e\,Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.[18]



17

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-166191 and CCDC-166192. 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).

Acknowledgement

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

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Received: July 12, 2001 [F3411]

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