Cascade Reactions of β-Amino-Substituted α,β-Unsaturated Fischer Carbene Complexes with 1,5-Dien-3-ynes as a Convenient Access to Ring-Annelated Benzene Derivatives

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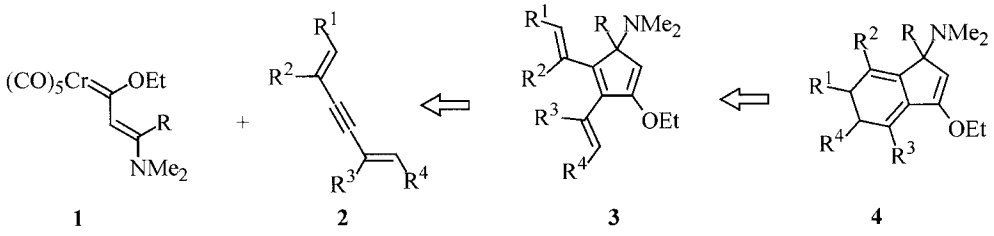
Upon heating pentacarbonyl(3-dimethylamino-1-ethoxypropenylidene)chromium complexes **1** with 1,5-dien-3-ynes **2** in pyridine at 80 °C, benzene-annelated cyclopentenones **8** and their regioisomers **9**, resulting from a sequence of cocyclization, 6π-electrocyclization and hydrolysis, were isolated in 12–75 % yield (13 examples). The more flexible the alkenyl substituents were in the dienynes **2**, the longer were the reaction times needed to achieve good chemical yields. This new cascade reaction of Fischer carbene complexes provides a direct route to trindanone analogues under milder conditions than traditional methods, and is compatible with more functionalities. Compounds **14** and **15** with steroid-like skeletons were thus prepared in 54–77 % yields (4 examples) from complex **1**-*i*Pr and the bicyclic alkyne **2**. Hexacycles **17** and **18** were accessible with high diastereoselectivity in the triquinane moiety by the same method in 45 % yield,

Introduction

Constructions of six-membered carbocycles by 6π-electrocyclizations of (*E,Z,E*)-1,3,5-hexatrienes, assembled either by a twofold Heck coupling of a 1,2-dihalocycloalkene with two identical alkenes[1] or by a Stille–Heck coupling sequence with an alkenylstannane and an alkene, respectively, on 2-bromocyclohex-1-enyl triflates,[2] have been developed and promoted by us[3] and other groups[4] in recent years. By this methodology, various 2,3-disubstituted 2,3,5,6,7,8-hexahydro- and 5,6,7,8-tetrahydronaphthalene derivatives were obtained from cyclohexene derivatives with two vicinal leaving groups, in good to excellent yields.[3] With this experience in mind, we conceived the possibility to access ethoxycyclopentene-annelated cyclohexadienes **4** by 6π-electrocyclization of 1,2-dialkenyl-substituted [(dimethylamino)ethoxy]cyclopentadienes **3**, which ought to be easily assembled by [3+2] cocyclization of β-dimethylamino-substituted α,β-unsaturated Fischer carbene-chromium complexes **1** and 1,5-dien-3-ynes **2** in pyridine, according to our previously published general protocol (Scheme 1).[5] Therefore, we set out to prepare various 1,5-dien-3-ynes and examined the possibility to construct oligosubstituted dihydroindene derivatives of type **4**.



1 **2** **3** **4**

Scheme 1. Conceived synthesis of 1,2-dialkenyl-5-dimethylamino-3-ethoxycyclopentadienes **3** and their 6π-electrocyclization to six-ring annelated protected cyclopentenones **4**.

Results and Discussion

Various 1,5-dien-3-ynes of type **2** were easily prepared by Sonogashira coupling of an alkenyl halide or an enol triflate **5** with a terminal alkyne **6** (Scheme 2).[6] Unfortunately,

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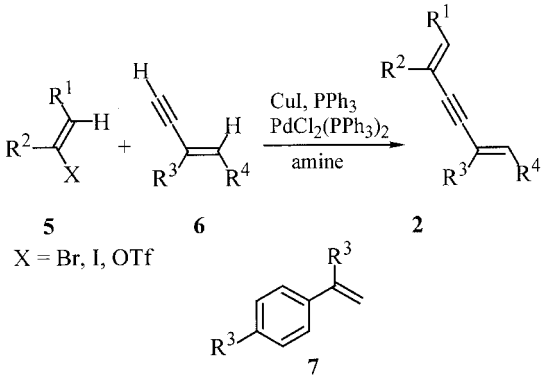
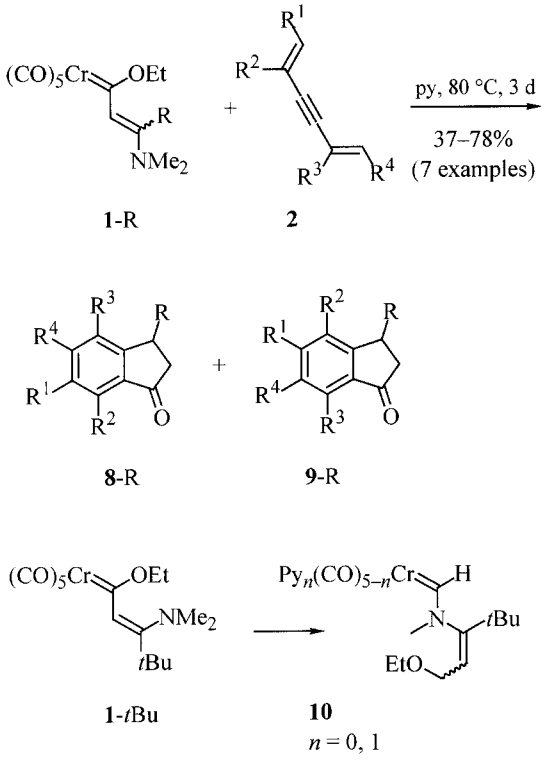
substituted styrene derivatives **7** were observed as byproducts and at least in one case even isolated (Entry 2 in Table 1). They were obviously formed by a palladium-catalyzed formal [4+2] cycloaddition of one enyne to another one as has been systematically studied by Yamamoto et al.[7] The formation of **7h** from 2-methylbut-1-en-3-yne (**6h**) could be suppressed by lowering the reaction temperature and shortening the time. However, the low chemical yield of **2fi** was probably due to the formation of the corresponding styrene derivative **7i** as the major product from 1-buten-3-yne (**6i**), however, in the applied workup procedure **7i** was not isolated and therefore not quantified.



Scheme 2. Synthesis of various 1,5-dien-3-ynes **2**. For details see Table 1.

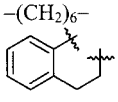
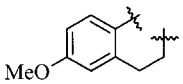
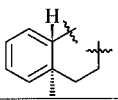


Scheme 3. Synthesis of indanone derivatives **8**-R and **9**-R. For details see Table 2.

Upon heating complexes **1** with conjugated dienynes **2** in pyridine at 80 °C for 3 d, only the indenone derivatives **8**-R/**9**-R, apparently arising from sequential cocyclization, 6π-electrocyclization, elimination of dimethylamine and hydrolysis, were obtained, instead of the expected dihydroindenes **4** (Scheme 3).

According to the previously reported systematic study,[5b] the regioselectivity in the cocyclization to yield cyclopentadienes **3** depends upon the steric demand and the electronic properties of the substituents on the alkyne, and the former plays a more important role than the latter. This is again confirmed by the current results. With two different substit-

Table 1. Preparation of 1,5-dien-3-ynes **2** by Sonogashira coupling of alkenyl halides or enol triflates **5** with terminal alkynes **6** (see Scheme 2).

Entry	Starting alkene	R^1	R^2	X	Starting alkyne	R^3	R^4	Product	Yield (%)
1	**5a**	$-(CH_2)_3-$		Br	**6a**	$-(CH_2)_3-$		**2aa**	71
2	**5a**	$-(CH_2)_3-$		Br	**6h**	Me	H	**2ah**	81[a]
3	**5b**	$-(CH_2)_4-$		I	**6h**	Me	H	**2bh**	84
4	**5b**	$-(CH_2)_4-$		I	**6b**	$-(CH_2)_4-$		**2bb**	92
5	**5c**	$-O(CH_2)_3-$		Br	**6b**	$-(CH_2)_4-$		**2cb**	75
6	**5d**	$-(CH_2)_6-$		Br	**6h**	Me	H	**2dh**	66
7	**5e**			Br	**6h**	Me	H	**2eh**	73
8	**5f**			Br	**6i**	H	H	**2fi**	11
9	**5f**			Br	**6h**	Me	H	**2fh**	68
10	**5f**			Br	**6j**	*t*Bu	H	**2fj**	92
11	**5g**			OTf	**6h**	Me	H	**2gh**	85
12	**5g**			OTf	**6j**	*t*Bu	H	**2gj**	76

[a] In addition, 13% of 4-methyl-(1′-propenyl)benzene was obtained.

Table 2. One-pot access to indanone derivatives **8**-R and **9**-R (see Scheme 3).

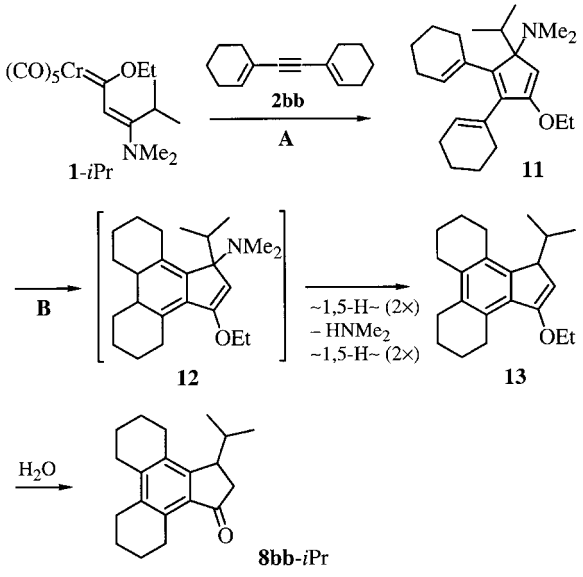
Entry	Complex **1**-R	Alkyne **2**	R^1	R^2	R^3	R^4	Product	Ratio **8**:**9**	Yield (%)
1	**1**-*c*Pr	**2hh**	H	Me	Me	H	**8hh**-*c*Pr	–	22
2	**1**-*i*Pr	**2hh**	H	Me	Me	H	**8hh**-*i*Pr	–	70
3	**1**-*c*Pr	**2ah**	$-(CH_2)_3-$		Me	H	**8ah**-*c*Pr + **9ah**-*c*Pr	1:1.1	16
4	**1**-*i*Pr	**2ah**	$-(CH_2)_3-$		Me	H	**8ah**-*i*Pr + **9ah**-*i*Pr	1.1:1	51
5	**1**-*t*Bu	**2ah**	$-(CH_2)_3-$		Me	H	**8ah**-*t*Bu + **9ah**-*t*Bu	1:1.1	37
6	**1**-*c*Pr	**2aa**	$-(CH_2)_3-$		$-(CH_2)_3-$		**8aa**-*c*Pr	–	19
7	**1**-Me	**2aa**	$-(CH_2)_3-$		$-(CH_2)_3-$		**8aa**-Me	–	12
8	**1**-*i*Pr	**2aa**	$-(CH_2)_3-$		$-(CH_2)_3-$		**8aa**-*i*Pr	–	75
9	**1**-*i*Pr	**2bh**	$-(CH_2)_4-$		Me	H	**8bh**-*i*Pr + **9bh**-*i*Pr	1.1:1	46
10	**1**-*t*Bu	**2bh**	$-(CH_2)_4-$		Me	H	**8bh**-*t*Bu + **9bh**-*t*Bu	1.1:1	21
11	**1**-*i*Pr	**2bb**	$-(CH_2)_4-$		$-(CH_2)_4-$		**8bb**-*i*Pr	–	68[a]
12	**1**-*t*Bu	**2bb**	$-(CH_2)_4-$		$-(CH_2)_4-$		**8bb**-*t*Bu	–	19[a]
13	**1**-*i*Pr	**2cb**	$-O(CH_2)_3-$		$-(CH_2)_4-$		**8cb**-*i*Pr + **9cb**-*i*Pr	1.1:1	67[a]
14	**1**-*i*Pr	**2dh**	$-(CH_2)_6-$		Me	H	**8dh**-*i*Pr + **9dh**-*i*Pr	–	0

[a] Reaction time 4 d.

uents of similar size on the dienynes **2**, two isomers **8**-R and **9**-R were formed with virtually no regioselectivity. The unsymmetrical dienyne **2bc** with one dihydropyrane and one cyclohexene moiety on the triple bond also gave both regioisomers **8bc**-*i*Pr and **9bc**-*i*Pr upon cocyclization with **1**-*i*Pr in a ratio of 1:1.1. Unfortunately, good chemical yields apparently can only be achieved with the isopropyl-substituted complex **1**-*i*Pr and to a lesser extent, the *tert*-butyl analogue **1**-*t*Bu. The more flexible the alkenyl substituents were in the dienynes **2**, the longer were the reaction times needed to complete the conversion. With a cyclooctenyl substituent as in **2dh** employed with **1**-*i*Pr, none of the cascade reaction products **8dh**-*i*Pr/**9dh**-*i*Pr and not even the corresponding cyclopentadiene of type **3** was observed.

When complex **1**-*t*Bu was employed, besides the indanone derivatives **8**/**9**, alkenylaminocarbene complexes of type **10** were formed in these reactions (Scheme 3).[8] This isomerization apparently competes with the formal [3+2] cycloaddition, and this is the major reason for lower chemical yields of the corresponding cocyclization products in certain cases (Entries 5, 10 and 12, Table 2).

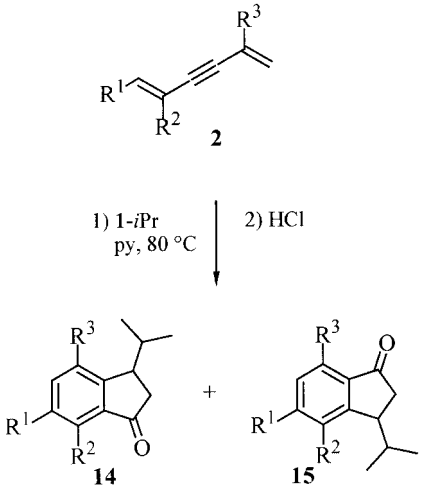
It is quite remarkable that the 6π-electrocyclization of the dialkenylcyclopentadienes of type **11**, which are initially formed in the formal [3+2] cycloaddition of e. g. complex **1**-*i*Pr to the dienyne **2bb** (Scheme 4), apparently proceeds with a comparable rate as the formation of **11** at 80 °C. The thus formed trisannelated cyclohexadiene **12**, by two consecutive 1,5-hydrogen shifts and elimination of dimethylamine followed by another two consecutive 1,5-hydrogen shifts eventually yields the more stable aromatic compound **13**.[9,10] The basic conditions certainly promote this elimination. The ^{1}H- and ^{13}C-NMR spectra of the crude product clearly show the ethoxy group of the vinyl ether moiety **13**. However, upon chromatography **13** obviously undergoes rapid hydrolysis so that the ketone **8bb**-*i*Pr was the only isolated product. In a control experiment, the complex **1**-*i*Pr was heated with the alkyne **2bb** in pyridine for only 40 h. After removal of $[Cr(CO)_5Py]$ and the starting material **2bb** by chromatography, an inseparable mixture was obtained, in which the initial cocyclization product **11** and the final indanone **8bb**-*i*Pr were identified as major components.



Scheme 4. Mechanistic rationalization of the formation of indanone derivatives of type **8bb**-*i*Pr. **A**: formal [3+2] cycloaddition. **B**: 6π-electrocyclization.

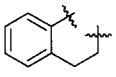
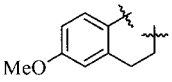
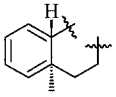
Trisannelated benzene derivatives, such as trindane and dodecahydrotriphenylene, were first reported by Wallach and by Mannich as minor products of acid-catalyzed cyclizing aldol condensations of cyclopentanone and cyclohexanone, respectively.[11] The chemical and physical properties of these compounds and their analogues have been studied extensively to examine the bond length alternation.[12] While a significant perturbation of aromaticity attributable to the so-called Mills–Nixon effect[13a] has not been observed,[13b,13c] trisannelated arenes of this type have offered opportunities for the synthesis of complex natural products.[14] However, very few procedures are available for target-oriented preparations of such trisannelated benzene derivatives, and most of them are carried out under harsh conditions, e. g. in strongly acidic solution or at high temperature.[15] Trindanone is accessible by further oxidation of trindane, and it has been regarded as a potential key intermediate in a rational synthesis of fullerene.[16] Cocyclizations of Fischer carbene complexes of type **1** with appropriately substituted dienynes as developed here provide accesses to trisannelated benzene derivatives with additional functionalities under much milder conditions than the traditional methods.

By the same methodology, tetracyclic steroid-like structures **14/15** are accessible from complex **1**-*i*Pr and annelated dienynes **2** (Scheme 5).[17] In these cases, hydrolysis of the initially formed five-membered ring enol ethers had to be enforced by addition of hydrochloric acid to the reaction mixture after removal of the solvent pyridine. Products **14** and **15** were thus obtained with almost no regioselectivity. With a *tert*-butyl substituent on the dienyne as in **2fj** and **2gj**, the cocyclization products were not formed.

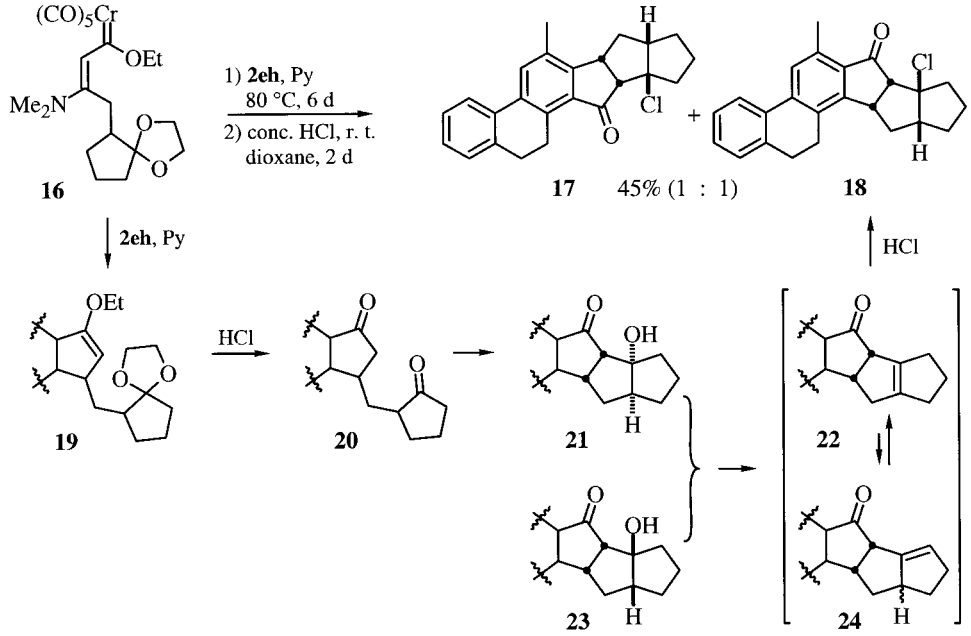


Scheme 5. Synthesis of tetracyclic compounds **14/15** with steroid-like skeletons via complex **1**-*i*Pr and 1,5-dien-3-ynes **2**. For details see Table 3.

Table 3. One-pot access to steroid-like tetracyclic skeletons **14/15** (see Scheme 5).

Entry	Alkyne	R^1	R^2	R^3	Reaction time [d]	Product	Ratio **14**:**15**	Yield (%)
1	**2eh**			Me	3	**14eh**-*i*Pr + **15eh**-*i*Pr	1.1:1	54
2	**2eh**			Me	6	**14eh**-*i*Pr + **15eh**-*i*Pr	1.1:1	77
3	**2fi**			H	6	**14fi**-*i*Pr + **15fi**-*i*Pr	1.3:1	66
4	**2fh**			Me	6	**14fh**-*i*Pr + **15fh**-*i*Pr	1.1:1	74
5	**2fj**			*t*Bu	6	**14fj**-*i*Pr + **15fj**-*i*Pr	–	0
6	**2gh**			Me	5	**14gh**-*i*Pr + **15gh**-*i*Pr	1.3:1[a]	72
7	**2gj**			*t*Bu	6	**14gj**-*i*Pr + **15gj**-*i*Pr	–	0

[a] Diastereomer ratio (1.2:1) in each regioisomer.



Scheme 6. Access to hexacycles **17/18** in a one-pot operation from complex **16** and dienyne **2eh**. The mechanistic details are shown for one of the two regioisomers only.

Starting from the carbene complex **16** with a protected carbonyl group in a cyclopentyl substituent and the dihydronaphthalene-annelated dienyne **2eh**, a 1:1 mixture of the hexacycles **17/18** also was obtained in a one-pot operation. The triquinane portions of the molecules **17/18** were formed with high diastereoselectivity (Scheme 6). The initially expected aldol products **21** and **23** were not observed.[18] Since the relative configurations of the hexacycles with their four stereogenic centers could not be assigned unambiguously based on the ^{1}H-, ^{13}C-, and even NOESY-2D-NMR spectra, crystals were grown by slow diffusion crystallization from diethyl ether/pentane. The X-ray crystal structure analysis (Figure 1)[19] then rigorously established the molecule as the hexacyclic chloride **17** with *cis*,*syn*,*cis*-configuration in the triquinane moiety.

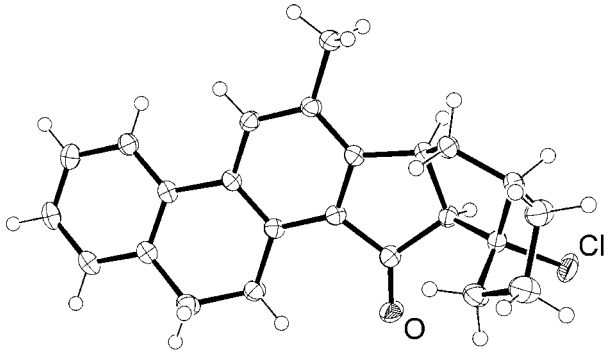


Figure 1. Structure of the hexacycle **17** in the crystal.[19]

Apparently, the initial cocyclization product **19** from the complex **16** and the dienyne **2eh** is hydrolyzed under the acidic conditions to yield the diketone **20**, which undergoes an intramolecular aldol reaction to furnish the diastereomeric triquinane derivatives **21** and/or **23**, most probably predominantly **21** with *cis*,*anti*,*cis*-configuration.[18] Dehydration of the alcohols **21** and/or **23** then would afford the alkenes **22** and/or **24**, subsequent addition of hydrogen chloride to the double bond in **22** and/or **24** would eventually yield the final products **17** and **18**.

Conclusions

Reaction of β-amino-substituted α,β-unsaturated Fischer carbene complexes of type **1** with 1,5-dien-3-ynes affords indanone derivatives **8**-R/**9**-R, even steroid-like skeletons **14/15**. Further elaboration of molecular complexity can be brought about by employing complexes like **16** which, after cocyclization with dienynes such as **2eh**, lead to hexacyclic skeletons such as **17/18**. However, improved regioselectivity would be desirable.

Experimental Section

General: ^{1}H and ^{13}C NMR: Bruker AM 250 (250 and 62.9 MHz) or Bruker AMX 300 (300 and 75 MHz). IR: Bruker IFS 66 (FT-IR). Low-resolution EI-MS: Varian MAT CH 7, MAT 731, ionizing voltage 70 eV. High-resolution EI-MS (HR EIMS): Varian MAT 311 A. X-ray crystal structure determination: The data were collected with a Stoe–Siemens-AED diffractometer. Melting points were determined with a Büchi melting point apparatus and are uncorrected. Elemental analysis: Mikroanalytisches Laboratorium des Instituts für Organische und Biomolekulare Chemie der Georg-August-Universität Göttingen. Chromatography: Merck silica gel 60 (230–400 mesh) or ICN neutral alumina (Super I, activity II). Solvents for chromatography were technical grade and freshly distilled before use. Tetrahydrofuran was distilled from sodium benzophenone ketyl, and pyridine was distilled from calcium hydride. Pentacarbonyl[(2*E*)-3-cyclopropyl-3-dimethylamino-1-ethoxy-2-propen-

1-ylidene]chromium (**1**-*c*Pr),[5b] pentacarbonyl[(2*E*)-3-dimethylamino-1-ethoxy-2-buten-1-ylidene]chromium (**1**-Me),[5b] pentacarbonyl[(2*E*)-3-dimethylamino-1-ethoxy-4-methyl-2-penten-1-ylidene]chromium (**1**-*i*Pr),[5b] pentacarbonyl[(2*Z*)-3-dimethylamino-1-ethoxy-4,4-dimethyl-2-penten-1-ylidene]chromium (**1**-*t*Bu),[5b] 1-bromo-1-cyclopentene (**5a**),[20] 1-bromo-1-cyclohexene (**5b**),[20] 5-bromo-3,4-dihydro-2*H*-pyran (**5c**),[20] 3-bromo-1,2-dihydronaphthalene (**5e**),[21] 2-bromo-6-methoxy-3,4-dihydro-2*H*-naphthalen-1-one,[22] 2-bromo-6-methoxy-1,2,3,4-tetrahydronaphthalen-1-ol,[21] (–)-4a-methyl-4,4a,5,6,7,8-hexahydro-3*H*-naphthalen-2-one,[23] 1-ethynyl-1-cyclopentene (**6a**),[24] 2-methyl-1-buten-3-yne (**6h**),[24] 1-ethynyl-1-cyclohexene (**6b**),[24] 1-buten-3-yne (**6i**),[24] 2,5-dimethyl-1,5-hexadien-3-yne (**2hh**),[25] pentacarbonyl[(2*E*)-4-(1′,4′-dioxaspiro[4.4]non-6′-yl)-3-dimethylamino-1-ethoxy-2-buten-1-ylidene]-chromium (**16**)[18] were prepared according to published procedures.

General Procedure for the Preparation of Internal Alkynes 2 by the Sonogashira Coupling (GP1): To an amine solution (50 mL) of the respective terminal alkyne **6** (100 mmol) and alkenyl halide **5** (100 mmol) in a screw-capped Pyrex bottle is added 200 mg of [dichlorobis(triphenylphosphane)palladium(II) [$PdCl_2(PPh_3)_2$], 500 mg of copper(I) iodide (CuI), and 150 mg of triphenylphosphane (PPh_3) at ambient temperature. The mixture is heated at 40–85 °C under argon for 4–18 h. After cooling to room temperature, the suspension is filtered through a 3 cm thick layer of Celite, and the Celite rinsed well with Et_2O (150 mL). The solvents from the filtrate are removed under reduced pressure, and the residue is subjected to chromatography on silica gel (150 g). Elution with pentane/Et_2O affords the coupling product **2**. Most of these 1,5-dien-3-ynes are not stable enough to prepare pure samples for elementary analyses, but they can be used for synthetic purposes without being analytically pure.

General Procedure for Cocyclizations of Complexes 1 with Alkynes 2 (GP2): A thick-walled, screw-cap Pyrex bottle equipped with a magnetic stirring bar is charged with a 0.05 M solution of the complex **1** in anhydrous pyridine. Dry argon is bubbled through the solution for 5 min, and 1.5 equiv. of the freshly prepared respective alkyne **2** is immediately added. The sealed bottle is kept in an oil bath at 80 °C for 3–6 d. The solvent is removed under reduced pressure, the residue is diluted with Et_2O, and the solution exposed to air for 2 h. After filtration and removal of solvent, the residue is purified by column chromatography on aluminum oxide (act. II).

3-Bromo-7-methoxy-1,2-dihydronaphthalene (5f): A solution of 2-bromo-6-methoxy-1,2,3,4-tetrahydronaphthalen-1-ol (prepared from 6-methoxy-1,2,3,4-tetrahydronaphthalen-1-one (25.0 g, 142 mmol) via 2-bromo-6-methoxy-1,2,3,4-tetrahydro-naphthalen-1-one without any serious purifications) in benzene (250 mL) was treated with a catalytic amount of *p*-toluenesulfonic acid monohydrate (540 mg), and the mixture was heated under reflux for 3 h using a Dean–Stark apparatus. After cooling to ambient temperature, a satd. solution of potassium carbonate (50 mL) was added to the mixture, and the aqueous phase was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were dried with $MgSO_4$. After evaporation of the solvents under reduced pressure, the residue was subjected to chromatography on silica gel (800 g). Elution with pentane/Et_2O/CH_2Cl_2 (18:1:1) gave 15.0 g (44%, based on the employed 6-methoxy-1,2,3,4-tetrahydronaphthalen-1-one) of **5f** [R_f — 0.70 (pentane/Et_2O, 9:1)] as a colorless solid, m.p. 41 °C. IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1} (C–H), 2934, 2833, 1626 (C=C), 1601, 1496, 1322, 1293, 1274, 1246, 1157, 1030, 873, 849, 828. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.76 (t, ^3J = 8.2 Hz, 2 H, 2-H), 2.95 (t, ^3J = 8.2 Hz, 2 H, 1-H), 3.01 (s, 3 H, OCH_3), 6.69–6.78 (m, 3 H, 4,6,8-H), 6.92 (d, ^3J = 8.2 Hz, 1 H, 5-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 29.5, 33.3 (–, C-1,2), 55.1 (+, OCH_3), 111.0, 113.7, 126.5, 128.7 (+, C-4,5,6,8), 120.8, 126.9, 134.5, 158.8 (C_{quat}, C-3,7,9,10) ppm. MS (70 eV): *m*/*z* (%) = 240/239/238/237 (98/17/100/12) [M^+], 159 (52) [M^+ – Br], 144 (74) [M^+ – Br – CH_3], 128/127 (23/23), 116/115 (52/100), 63 (14). $C_{11}H_{11}BrO$ (239.1): calcd. C 55.25, H 4.64; found C 55.05, H 4.49.

2,2-Dimethyl-3-methylenpent-4-yne (6j): A 500 mL flask equipped with a magnetic stirring bar was charged with 3-hydroxy-2,2,3-trimethyl-4-pentyne (20.0 g, 158 mmol) and *p*-toluenesulfonic acid monohydrate (1.00 g). The reaction mixture was heated at 120 °C (oil bath temperature) and the product directly distilled from it. The crude product was dried with $MgSO_4$ and distilled again to afford 10.1 g (59%) of **6j** as a colorless oil, b. p. 98 °C.[26]

4-(1′-Cyclopentenyl-2-methylbut-1-en-3-yne (2ah) and 4-Methyl-(2′-propenyl)benzene (7h): Preparation according to GP1. To a solution of 1-bromo-1-cyclopentene (**5a**) (5.84 g, 39.7 mmol) in diisopropylamine (40 mL) was added PPh_3 (100 mg), LiCl (100 mg), CuI (75.0 mg), $PdCl_2(PPh_3)_2$ (100 mg) and finally 2-methylbut-1-en-3-yne (**6h**) (5.00 mL, 53.6 mmol), and the mixture was heated at 60 °C for 16 h. The suspension was diluted with pentane (100 mL) and washed with water (50 mL). The aqueous phase was extracted with pentane (50 mL). The combined organic phases were washed with water (30 mL) and hydrochloric acid (1 N, 3 × 30 mL). The solution was dried with $MgSO_4$. After filtration, the solvents were removed under ambient pressure, and the residue was distilled under reduced pressure to afford 3.76 g of a colorless oil [b. p. 75 °C (20 Torr)], which contained **2ah** (90%) and 4-methyl-(2′-propenyl)benzene (10%). The amount of **2ah** corresponded to 3.38 g (64%). MS (70 eV): *m*/*z* (%) = 132 (100) [M^+], 117 (78) [M^+ – CH_3], 115 (58), 91 (64), 77 (14), 65 (16), 51 (10). **2ah**: ^1H NMR (250 MHz, $CDCl_3$): δ = 1.40–1.70 (m, 5 H, CH_3, 4′-H), 1.90 (m, 4 H, 3′,5′-H), 5.20–5.23 and 5.27–5.29 (m, 2 H, 4-H), 6.02 (m, 1 H, 2′-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 23.3 (–, C-4′), 23.5 (+, CH_3), 33.3, 36.3 (–, C-3′,5′), 85.7, 91.6 (C_{quat}, C-1,2), 121.2 (–, C-4), 124.4, 126.9 (C_{quat}, C-3,1′), 137.8 (+, C-2′) ppm. The NMR spectroscopic data of 4-methyl-(2′-propenyl)benzene agreed with the previously reported ones.[27]

Di(1′-cyclohexenyl)ethyne (2bb): (According to GP1). To a solution of 1-iodo-1-cyclohexene (**5b**) (5.82 g, 28.0 mmol) in diisopropylamine (30 mL) was added 1-ethynyl-1-cyclohexene (**6b**) (3.19 g, 30.0 mmol), $PdCl_2(PPh_3)_2$ (70.0 mg), PPh_3 (70.0 mg), CuI (50.0 mg), and LiCl (60.0 mg), and the mixture was heated at 40 °C for 5 h. After filtration of the mixture and evaporation of the solvents under reduced pressure, the residue was subjected to chromatography on silica gel (70 g). Elution with pentane gave 4.80 g (92%) of **2bb** [R_f — 0.75 (pentane)] as a colorless oil. The NMR spectroscopic data agreed with the previously reported ones.[28]

3-(3′-Methylbut-3′-en-1′-ynyl)-1,2-dihydronaphthalene (2eh): Preparation according to GP1. To a solution of 3-bromo-1,2-dihydronaphthalene (**5e**) (4.98 g, 23.8 mmol) in diisopropylamine (30 mL) was added PPh_3 (50 mg), CuI (50 mg), LiCl (50 mg), $PdCl_2(PPh_3)_2$ (60 mg), and 5.00 mL (53.6 mmol) of 2-methylbut-1-en-3-yne (**6h**), and the mixture was heated at 70 °C for 2 h. After filtration and evaporation of the solvents under reduced pressure, the residue was subjected to chromatography on silica gel (100 g). Elution with pentane gave 3.38 g (73%) of **2eh** [R_f — 0.36 (pentane)] as a colorless oil. IR (film): $\tilde{\nu}$ = 3094 cm^{-1} (C–H), 3065, 3015, 2942, 2889, 2835, 2190 (C≡C), 1615 (C=C), 1484, 1453, 1428, 1372, 1305, 889, 748. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.04 (s, 3 H, CH_3), 2.53 (t, ^3J = 7.5 Hz, 2 H, 2-H), 2.91 (t, ^3J = 7.5 Hz, 2 H, 1-

H), 5.33–5.35 and 5.42–5.43 (m, 2 H, 4′-H), 6.86 (s, 1 H, 4-H), 7.08–7.23 (m, 4 H, 5,6,7,8-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 23.5 (+, CH_3), 27.5, 27.7 (–, C-1,2), 89.9, 92.6 (C_{quat}, C≡C), 121.0, 126.9, 133.7, 134.7 (C_{quat}, C-3,9,10,3′), 121.7 (–, C-4′), 126.3, 126.6, 127.4, 127.6, 133.1 (+, C-4,5,6,7,8) ppm. MS (70 eV): *m*/*z* (%) = 194 (100) [M$^+$], 178 (40), 165 (10), 152 (12), 128 (14), 115 (12). $C_{15}H_{14}$ (194.3): calcd. C 92.74, H 7.26; found C 92.84, H 7.02.

(4a*R*)-4a-Methyl-7-(3′-methylbut-3′-en-1′-ynyl)-1,2,3,4,4a,5,6,8a-octahydronaphthalene (2gh): Preparation according to GP1. To a solution of (4a*R*)-4a-methyl-3,4,4a,5,6,7,8,8a-octahydronaphthalen-2-yl trifluoromethanesulfonate (**5g**) (4.47 g, 15.0 mmol) in DMF (40 mL) was added PPh_3 (50 mg), CuI (50 mg), LiCl (50 mg), $PdCl_2(PPh_3)_2$ (60 mg), NEt_3 (1.52 g, 15.0 mmol) and 2-methylbut-1-en-3-yne (**6h**) (4.00 mL, 42.9 mmol), and the mixture was heated at 50 °C for 12 h. The reaction mixture was diluted with 50 mL of pentane/Et_2O (1:1) and washed with water (200 mL). The aqueous phase was extracted with pentane/Et_2O (1:1; 4 × 50 mL). The combined organic phases were washed with water (30 mL) and hydrochloric acid (1 N, 30 mL). The solution was dried with $MgSO_4$. After filtration and evaporation of the solvents under reduced pressure, the residue was subjected to chromatography on silica gel (100 g). Elution with pentane gave 2.74 g (85%) of **2gh** [R_f — 0.63 (pentane)] as a colorless oil. IR (film): $\tilde{\nu}$ = 2922 cm^{-1} (C–H), 2855, 2188 (C≡C), 1671 (C=C), 1608, 1446, 1373, 891. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.80 (s, 3 H, CH_3), 1.02–1.57 (9 H) and 1.68–2.05 (4 H) (m, total 13 H, 1,2,3,4,5,6,8a-H), 1.89 (s, 3 H, CH_3), 5.16–5.18 and 5.22–5.24 (m, 2 H, 4′-H), 5.98–6.01 (m, 1 H, 8-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 16.3 (+, CH_3), 22.1, 26.6, 28.4, 34.0, 40.9, 42.6 (–, C-1,2,3,4,5,6), 23.6 (+, CH_3), 31.5 (C_{quat}, C-4a), 39.9 (+, C-8a), 87.9, 89.9 (C_{quat}, C≡C), 119.7, 127.0 (C_{quat}, C-7,3′), 120.8 (+, C-8), 133.7 (–, C-4′) ppm. MS (70 eV): *m*/*z* (%) = 214 (100) [M$^+$], 199 (59) [M$^+$ – CH_3], 185 (10), 171 (23), 157 (34), 143 (30), 131 (20), 118 (96), 95 (29), 91 (38), 81 (50), 77 (21), 67 (39), 55 (29), 53 (14), 41 (36). $C_{16}H_{22}$ (214.4): calcd. C 89.65, H 10.35; found C 89.99, H 10.97.

3-Isopropyl-4,7-dimethylindan-1-one (8hh-*i*Pr): Preparation according to GP2. To a solution of complex **1**-*i*Pr (723 mg, 2.00 mmol) in pyridine (40 mL) was added 2,5-dimethylhexa-1,5-dien-3-yne (**2hh**) (531 mg, 5.00 mmol), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (act. II, 40 g) eluting with pentane/Et_2O (from 1:0 to 3:1) gave 282 mg (70%) of **8hh**-*i*Pr [R_f = 0.65 (pentane/Et_2O, 3:1)] as a colorless oil. IR (film): $\tilde{\nu}$ = 2984 cm^{-1} (C–H), 1705 (C=O), 1581, 1495, 1248, 821. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.37 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.02 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 2.23–2.37 (m, 1 H, *i*Pr-H), 2.31 (s, 3 H, CH_3), 2.44–2.47 (m, 2 H, 2-H), 2.53 (s, 3 H, CH_3), 3.35 (qui, ^3J = 7.9, ^3J = 7.9, ^3J = 7.9 Hz, 1 H, 3-H), 6.94 (d, ^3J = 7.5 Hz, 1 H, 5-H), 7.16 (d, ^3J = 7.5 Hz, 1 H, 6-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.7 (+, *i*Pr-C), 17.7, 17.8 (+, CH_3), 21.6 (+, *i*Pr-C), 29.0 (+, *i*Pr-C), 38.2 (–, C-2), 42.5 (+, C-3,4), 129.2, 135.2 (+, C-5,6), 132.2, 134.3, 135.3, 156.6 (C_{quat}, C-3a,4,7,7a), 207.9 (C_{quat}, C-1,2,5,6) ppm. MS (70 eV): *m*/*z* (%) = 202 (48) [M$^+$], 160 (41), 159 (100) [M$^+$ – C_3H_7], 129 (10), 116 (12), 115 (16), 91 (10). $C_{14}H_{18}O$ (202.3): calcd. C 83.12, H 8.97; found C 82.80, H 8.69.

3-Isopropyl-4-methyl-3,6,7,8-tetrahydro-2*H*-*as*-indacen-1-one (8ah-*i*Pr) and 1-Isopropyl-4-methyl-1,6,7,8-tetrahydro-2*H*-*as*-indacen-3-one (9ah-*i*Pr): Preparation according to GP2. To a solution of complex **1**-*i*Pr (723 mg, 2.00 mmol) in pyridine (40 mL) was added 4-(1′-cyclopentenyl)-2-methylbut-1-en-3-yne (**2ah**) (651 mg; 4.43 mmol; 90% purity) and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (act. II, 40 g) eluting with pentane/Et_2O (from 1:0 to 3:1) gave 231 mg (51%) of **8ah**-*i*Pr and **9ah**-*i*Pr [R_f = 0.64 (pentane/Et_2O, 3:1); ratio 1.1:1] as a pale-yellow oil. IR (film): $\tilde{\nu}$ = 2960 cm^{-1} (C–H), 1706 (C=O), 1609, 1465, 1399, 1269, 736. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.41, 0.46 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.03, 1.04 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 2.00–2.57 (m, 5 H, 2,7-H and *i*Pr-H), 2.33, 2.56 (s, 3 H, CH_3), 2.78–2.92 (m, 3 H) and 3.12–3.18 (m, 1 H) [total 4 H, 6,8-H], 3.30–3.32, 3.39–3.41 (m, 1 H, 3-H of **8ah**-*i*Pr and 1-H of **9ah**-*i*Pr), 6.95, 7.20 (s, 1 H, 5-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.8, 14.9, 18.1, 18.3 (+, *i*Pr-C), 21.8, 22.1 (+, CH_3), 25.2, 25.3 (–, C-7), 28.7, 29.1 (+, *i*Pr-C), 30.5, 30.6, 31.5, 32.8 (–, C-6,8), 37.9, 38.0 (–, C-2), 42.8, 43.2 (+, C-3 of **8ah**-*i*Pr and C-1 of **9ah**-*i*Pr), 125.5, 131.6 (+, C-5), 132.7, 132.9, 133.1, 136.5, 138.1, 139.7, 144.5, 151.5, 154.3 × 2 (C_{quat}, Ar-C), 207.3, 207.8 (C_{quat}, CO) ppm. MS (70 eV): *m*/*z* (%) = 228 (40) [M$^+$], 186 (25), 185 (100) [M$^+$ – C_3H_7]. $C_{16}H_{20}O$ (228.3): calcd. C 84.16, H 8.83; found C 83.96, H 8.68.

3-Isopropyl-2,3,4,5,6,7,8,9-octahydrotrinden-1-one (8aa-*i*Pr): Preparation according to GP2. To a solution of complex **1**-*i*Pr (723 mg, 2.00 mmol) in pyridine (40 mL) was added di(1-cyclopentenyl)ethyne (**2aa**) (633 mg, 4.00 mmol), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (act. II, 40 g) eluting with pentane/Et_2O (from 1:0 to 3:1) gave 382 mg (75%) of **8aa**-*i*Pr [R_f = 0.63 (pentane/Et_2O, 3:1)] as a colorless solid, m.p. 121–122 °C. IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1} (C–H), 1695 (C=O), 1588, 1448, 1281, 1126. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.43 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.98 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.94–2.22 (m, 4 H, 5,8-H), 2.23–2.48 (m, 3 H, *i*Pr-H, 2-H), 2.69 (t, ^3J = 7.6 Hz, 2 H), 2.76 (t, ^3J = 7.9 Hz, 2 H), 2.87 (t, ^3J = 7.7 Hz, 2 H), and 3.11 (t, ^3J = 7.4 Hz, 2 H) [total 8 H, 4,6,7,9-H], 3.20–3.35 (m, 1 H, 3-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.6, 21.6 (+, *i*Pr-C), 25.0 × 2 (–, C-5,8), 28.5 (+, *i*Pr-C), 30.0, 30.4, 30.6, 31.2 (–, C-4,6,7,9), 37.4 (–, C-2), 43.2 (+, C-3), 131.4, 138.2, 139.6, 140.6, 147.0, 151.7 (C_{quat}, Ar-C), 206.6 (C_{quat}, C-1) ppm. MS (70 eV): *m*/*z* (%) = 254 (26) [M$^+$], 211 (100) [M$^+$ – C_3H_7]. $C_{18}H_{22}O$ (254.4): calcd. C 84.99, H 8.72; found C 84.74, H 8.50.

3-Isopropyl-2,3,4,5,6,7,8,9,10,11-decahydrocyclopenta[*l*]phenanthren-1-one (8bb-*i*Pr): Preparation according to GP2. To a solution of complex **1**-*i*Pr (723 mg, 2.00 mmol) in pyridine (40 mL) was added di(1-cyclohexenyl)ethyne (**2bb**) (745 mg, 4.00 mmol), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide (act. II, 40 g) eluting with pentane/Et_2O (from 1:0 to 3:1) gave 382 mg (68%) of **8bb**-*i*Pr [R_f = 0.73 (pentane/Et_2O, 3:1)] as a colorless solid, m.p. 148–149 °C. IR (KBr): $\tilde{\nu}$ = 2931 cm^{-1} (C–H), 1692 (C=C), 1571, 1546, 1278, 1124. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.41 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.04 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.50–2.10 (m, 8 H, 5,6,9,10-H), 2.22–2.82 (m, 9 H, *i*Pr-H, 4,7,8,11-H), 3.08–3.23 (m, 2 H, 2-H), 3.23–3.35 (m, 1 H, 3-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.6, 22.0 (+, *i*Pr-C), 21.8, 22.1, 22.6, 22.8, 25.9, 26.3, 26.4, 27.2 (–, C-4,5,6,7,8,9,10,11), 28.5 (+, *i*Pr-C), 38.4 (–, C-2), 42.0 (+, C-3), 131.4, 131.4, 134.1, 134.7, 142.3, 154.7 (C_{quat}, Ar-C), 207.8 (C_{quat}, C-1) ppm. MS (70 eV): *m*/*z* (%) = 282 (54) [M$^+$], 239 (100) [M$^+$ – C_3H_7]. $C_{20}H_{26}O$ (282.4): calcd. C 85.06, H 9.28; found C 84.84, H 9.34.

17-Isopropyl-12-methyl-6,7,16,17-tetrahydrocyclopenta[*a*]phenanthren-15-one (14eh-*i*Pr) and 15-Isopropyl-12-methyl-6,7,15,16-tetrahydrocyclopenta[*a*]phenanthren-17-one (15eh-*i*Pr). Variant A: Preparation according to GP2. To a solution of complex **1**-*i*Pr (723 mg, 2.00 mmol) in pyridine (40 mL) was added 3-(3′-methylbut-3′-en-1′-ynyl)-1,2-dihydronaphthalene (**2eh**) (583 mg 3.00 mmol) and the mixture was stirred at 80 °C for 3 d. After dilution with Et_2O,

concd. hydrochloric acid was added to the reaction mixture (< pH 2). Chromatography on aluminum oxide (act. II, 40 g) eluting with pentane/Et_2O (from 1:0 to 3:1) gave 313 mg (54%) of **14eh**-*i*Pr and **15eh**-*i*Pr (ratio 1.1:1) as a semi-solid. **14eh**-*i*Pr could be isolated in pure form by chromatography on silica gel (60 g) eluting with pentane/Et_2O (5:1).

Variant B: Preparation according to GP2. To a solution of complex **1**-*i*Pr (871 mg, 2.41 mmol) in pyridine (48 mL) was added 3-(3′-methylbut-3′-en-1′-ynyl)-1,2-dihydronaphthalene (**2eh**) (702 mg, 3.61 mmol), and the mixture was stirred at 80 °C for 6 d. After dilution with Et_2O, concd. hydrochloric acid was added to the reaction mixture (< pH 2). Chromatography on aluminum oxide (act. II, 40 g) eluting with pentane/Et_2O (from 1:0 to 3:1) gave 540 mg (77%) of **14eh**-*i*Pr and **15eh**-*i*Pr **(**ratio 1.1:1) as a semi-solid.

14eh-*i*Pr: Colorless solid, m.p. 105 °C. IR (KBr): $\tilde{\nu}$ = 2952 cm^{-1} (C–H), 2930, 1695 (C=O), 1563, 1485, 1445, 1318, 1234, 1091, 913, 759. ^1H NMR (250 MHz, $CDCl_3$, plus HH-, CH-COSY, HMBC and NOESY): δ = 0.51 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.11 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 2.34–2.50 (m, 1 H, *i*Pr-H), 2.45 (s, 3 H, CH_3), 2.58–2.61 (m, 2 H, 16-H), 2.78–2.86 (m, 2 H, 7-H), 3.26–3.61 (m, 3 H, 6,17-H), 7.23–7.34 (m, 3 H, Ar-H), 7.71 (d, ^3J = 7.7 Hz, 1 H, Ar-H), 7.76 (s, 1 H, Ar-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.8, 22.0 (+, *i*Pr-C), 18.2 (+, CH_3), 21.8 (–, C-6), 27.9 (–, C-7), 29.2 (+, *i*Pr-C), 38.8 (–, C-16), 42.3 (+, C-17), 123.4, 126.7, 127.3, 127.9, 131.0 (+, Ar-C), 132.9, 133.2, 133.4, 134.0, 134.4, 137.1, 156.0 (C_{quat}, Ar-C), 208.2 (C_{quat}, CO) ppm. MS (70 eV): *m*/*z* (%) = 290 (51) [M^+], 247 (100) [$M^+ - C_3H_7$], 229 (11), 203 (16). $C_{21}H_{22}O$ (290.4): calcd. C 86.85, H 7.64; found C 87.10, H 7.88.

Mixture of 14eh-*i*Pr and 15eh-*i*Pr: A semi-solid. IR (film): $\tilde{\nu}$ = 2960 cm^{-1} (C–H), 1697 (C=O), 1585, 1565, 1445, 1265, 738. MS (70 eV): *m*/*z* (%) = 290 (64) [M^+], 247 (100) [$M^+ - C_3H_7$], 203 (22). $C_{21}H_{22}O$ (290.4): calcd. C 86.85, H 7.64; found C 86.58, H 7.38. **15eh-*i*Pr:** ^1H NMR (250 MHz, $CDCl_3$): δ = 0.44 (d, ^3J = 6.7 Hz, 3 H, *i*Pr-H), 1.11 (d, ^3J = 6.7 Hz, 3 H, *i*Pr-H), 2.21–2.28 (m, 1 H, *i*Pr-H), 2.70 (s, 3 H, CH_3), 2.56–2.97 (m, 6 H, 6,7,16-H), 3.41–3.50 (m, 1 H, 15-H), 7.23–7.34 (m, 3 H, Ar-H), 7.52 (s, 1 H, Ar-H), 7.78 (d, ^3J = 7.8 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.7, 22.0 (+, *i*Pr-C), 18.3 (+, CH_3), 23.9, 28.5 (–, C-6,7), 29.9 (+, *i*Pr-C), 38.5 (–, C-16), 42.2 (+, C-15), 124.5, 125.4, 126.9, 127.9, 128.2 (+, Ar-C), 131.4, 133.4, 133.6, 136.0, 137.7, 139.4, 156.1 (C_{quat}, Ar-C), 207.3 (C_{quat}, CO) ppm.

(±)-(3aα,3bα,12bα,13aα)-3a-Chloro-2,3,3a,3b,4,5,6,12b,13,13a-decahydro-12-methyl-1*H*-cyclopenta[1′,2′:4,5]pentaleno[2,1-*a*]phenanthrene-4-one (17) and (±)-(3aα,3bα, 12cα,13aα)-3a-Chloro-2,3,3a,3b,4,11,12,12c,13,13a-decahydro-5-methyl-1*H*-cyclopenta-[1′,2′:4,5]pentaleno[2,1-*a*]phenanthrene-4-one (18): Preparation according to GP2. To a solution of complex **16** (1.33 g, 2.90 mmol) in pyridine (58 mL) was added 3-(3′-methylbut-3′-en-1′-ynyl)-1,2-dihydronaphthalene (**2eh**) (839 mg, 4.32 mmol), and the mixture was stirred at 80 °C for 6 d. After oxidation, filtration and removal of the solvents, the residue was diluted with 1,4-dioxane (100 mL). To the solution was added concd. hydrochloric acid (< pH 1), and this reaction mixture was stirred at ambient temperature for 2 d. The solvents were removed under reduced pressure. Chromatography on silica gel (70 g) eluting with pentane/Et_2O (10:1) gave 471 mg (45%) of **17** and **18** (ratio 1:1) as a semi-solid. Compoune **17** could be isolated in pure form by careful chromatography on silica gel (120 g) eluting with pentane/Et_2O (10:1).

17: Colorless crystals, m.p. 135 °C. IR (KBr): $\tilde{\nu}$ = 2952 cm^{-1} (C–H), 2929, 1700 (C=O), 1483, 1444, 1315, 1215, 755. ^1H NMR (250 MHz, $CDCl_3$, plus HH-, CH-COSY, HMBC and NOESY): δ = 1.20–1.49 (2 H), 1.71–2.13 (4 H), 2.17–2.30 (1 H) [m, total 7 H, 1,2,3,13-H], 2.39 (s, 3 H, CH_3), 2.58 (d′′t′′, ^2J = 13.0, ^3J = 8.5, ^3J = 8.5 Hz, 1 H, 13-H), 2.72–2.88 (m, 2 H, 6-H), 2.96–3.06 (m, 1 H, 13a-H), 3.23–3.44 (m, 1 H, 5-H), 3.49–3.56 (m, 1 H, 5-H), 3.67 (d, ^3J = 8.8 Hz, 1 H, 3b-H), 4.01 (′′q′′, ^3J = 8.8, ^3J = 8.8, ^3J = 8.8 Hz, 1 H, 12b-H), 7.24–7.35 (3 H), 7.69 (d, ^3J = 7.4 Hz, 1 H, Ar-H), 7.73 (s, 1 H, 11-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 18.3 (+, CH_3), 21.9 (–, C-5), 23.6, 27.5, 37.8 (–, C-1,2,3), 28.1 (–, C-6), 37.2 (–, C-13), 43.2 (+, C-12b), 59.9 (+, C-13a), 64.0 (+, C-3b), 82.4 (C_{quat}, C-3a), 123.6, 126.9, 127.7, 128.2, 131.3 (+, Ar-C), 132.0, 132.8, 133.3, 134.8, 135.6, 137.4, 155.8 (C_{quat}, Ar-C), 205.7 (C_{quat}, CO) ppm. MS (70 eV): *m*/*z* (%) = 365/364/363/362/361 (8/34/28/100/9) [M^+], 326 (36) [M^+ – HCl], 245 (34), 229 (11), 215 (18), 79 (16). $C_{24}H_{23}ClO$ (362.9): calcd. C 79.43, H 6.39; found C 79.55, H 6.02.

Mixture of 17 and 18: Colorless crystals. IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1} (C–H), 2871, 1691 (C=O), 1584, 1559, 1443, 1338, 1256, 1227, 1010, 770, 732. MS (70 eV): *m*/*z* (%) = 365/364/363/362/361 (5/16/12/50/4) [M^+], 326 (100) [M^+ – HCl], 248 (43), 245 (20), 215 (10). $C_{24}H_{23}ClO$ (362.9): calcd. C 79.43, H 6.39; found C 79.77, H 6.17. **18:** ^1H NMR (250 MHz, $CDCl_3$): δ = 1.21–1.39 (2 H), 1.70–2.03 (4 H), 2.15–2.37 (1 H) [m, total 7 H, 1,2,3,13-H], 2.56 (d′′t′′, ^2J = 14.3, ^3J = 8.0, ^3J = 8.0 Hz, 1 H, 13-H), 2.67 (s, 3 H, CH_3), 2.70–3.04 (m, 5 H, 11,12,13a-H), 3.67 (d, ^3J = 8.8 Hz, 1 H, 3b-H), 4.08 (′′q′′, ^3J = 8.8, ^3J = 8.8, ^3J = 8.8 Hz, 1 H, 12c-H), 7.26–7.38 (m, 3 H, Ar-H), 7.52 (s, 1 H, 6-H), 7.79 (dd, ^3J = 8.3, ^4J = 1.2 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 18.3 (+, CH_3), 21.9 (–, C-5), 23.6, 27.5, 37.8 (–, C-1,2,3), 28.1 (–, C-6), 37.2 (–, C-13), 43.2 (+, C-12c), 59.9 (+, C-13a), 64.0 (+, C-3b), 82.4 (C_{quat}, C-3a), 124.6, 125.6, 127.1, 128.3, 128.7 (+, Ar-C), 131.0, 131.8, 133.4, 137.3, 137.7, 140.1, 155.9 (C_{quat}, Ar-C), 205.7 (C_{quat}, CO) ppm.

Supporting Information Available: Experimental procedures and spectroscopic data of all compounds not presented here (see footnote on the first page of this article and http://www.acs.org).

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