Steroid-Like Ring Skeletons by Cyclohexadiene Annulation to Enamines with Alkynylcarbene Complexes of Chromium and Tungsten via Pyran-2-ylidene Complexes†

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Abstract: A highly regioselective cyclohexadiene annulation to the C═C(N) bond of an enamine is achieved in two steps involving the condensation of a 1-alkynylcarbene complex $(CO)_5M$═C(OEt)C≡CPh **1** (M = Cr, W) with an enolizable carbonyl compound (2,4-pentanedione, 3-oxobutyric acid ester, 2-tetralones, and 1,3-cyclopentanedione) to give a pyran-2-ylidene complex **3**, **5**, and **17**, which on subsequent reaction with cyclic enamines **6**, **9**, **13**, and **16**, generate a 5-amino-1,3-cyclohexadiene by elimination of $M(CO)_6$. Thus, bicyclic ring skeletons **7** and **10**, steroid-like molecules **8**, **18**, and **19**, and tetracyclic compounds **11**, **12**, and **15** are obtained mostly in good chemical yields and under mild conditions. Side reactions, such as base-induced self-condensation of **3** to give aryl pyran-2-ylidene complexes **20** become efficiently suppressed in hydrocarbon solvents.

Reactions of alkynylcarbene complexes $(CO)_5M$═C(OEt)C≡CPh **1** (M = Cr, W) with carbon nucleophiles, e.g., enol ethers[2−4] or enamines[5,6] were found to provide a rich source of novel and synthetically useful routes to the generation of carbocyclic ring compounds. For example, it has been reported most recently that cyclopentadiene annulation products are obtained regioselectively and in high chemical yields by an overall [3+2] cycloaddition of compound **1** to tertiary 1-aminocycloalkenes (Scheme 1).[1,5d] The latter annulation process was shown to proceed via initial formation of 1-metalla-1,3,5-hexatrienes.[5] With respect to the apparent pivotal role of 1-metalla-1,3,5-hexatrienes in this and also in related processes, we are currently exploring different modes for the generation of such compounds as well as a manifold of different reaction paths by which 1-metalla-1,3,5-hexatrienes can be transformed into organic products. For example, cyclopentadiene complexes[7] as precursors to cyclopentadienes, 2,3-homopyrroles,[5b] pyran-2-ylidene complexes, and 1,2-dihydropyridin-2-ylidene complexes[5] may be generated depending on the substitution pattern and the reaction conditions employed.

An approach to 1-metalla-1,3,5-hexatrienes, other than by the "enamine route", is based on ring-opening reactions of pyran-2-ylidene complexes **3** (Scheme 2), e.g., through the addition of amines.[8] While attempting to extend this latter route to the formation of 1-metalla-1,3,5,7-tetraenes by reacting enamines (vinylogous amines) instead of amines with pyran-2-ylidene complexes, a fragmentation of the pyran-2-ylidene ring was found to occur. Addition of enamines to pyran-2-ylidene complexes led to an overall *cis*-annulation of a cyclohexadiene unit to the C═C(N) bond of the enamine by disengagement of $M(CO)_6$ (Scheme 1). This type of reaction has been reported (with very little experimental detail) by Wulff et al.[9] prior to our studies.

The cyclohexadiene annulation reaction via pyran-2-ylidene complexes is well suited for synthetical application, since it is highly regioselective, proceeds under very mild conditions, and affords good chemical yields if carried out under proper reaction conditions. We wish to report on a successful syntheses of, e.g., steroid-like molecules by a simple two-step procedures involving (a) the addition of an 1-alkynylcarbene complex **1** to an enolizable carbonyl component to generate a pyran-2-ylidene

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§ X-ray structure analysis.

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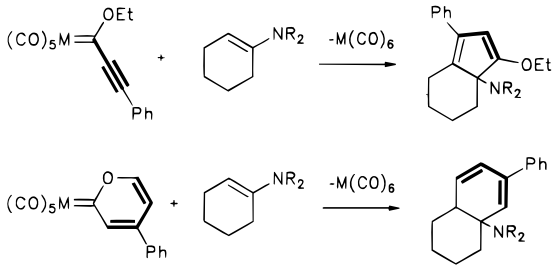
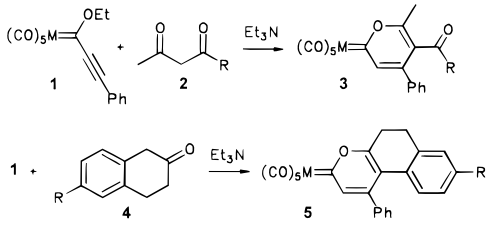
Scheme 1. Cyclopentadiene and Cyclohexadiene Annulation to Enamines (M = Cr, W)



Scheme 2. Pyran-2-ylidene Complexes by Condensation of Alkynylcarbene Complexes with Carbonyl Compounds



1 M	2 R	3 M	R	[3] %	4 R	5 M	R	[5] %
a Cr	a Me	a Cr	Me	91	a H	a Cr	H	88
b W	b OMe	b W	Me	90 [8]	b OMe	b Cr	OMe	76
		c W	OMe	85		c W	H	64
						d W	OMe	81

complex, which (b) is subsequently reacted with an enamine to give the cyclohexadiene annulation product.

Pyran-2-ylidene Complexes. Among several routes available for the generation of pyran-2-ylidene complexes[2c,3b,3c,3j,3k,5,8−16], the condensation of a 1-alkynylcarbene complex **1a**,**b** with an enolizable carbonyl compound, e.g., 2,4-pentanedione (**2**), was selected for the generation of complexes **3**.[9] If carried out under carefully controlled conditions, in pentane and in the presence of catalytic amounts of Et_3N, this reaction usually affords clean products in high yields that separate crystalline complexes directly from the reaction mixture.[8] Furthermore, condensation of **1** with carbonyl components other than 1,3-diketones proved to be possible with 2-tetralones **2** affording benzo[*d*]chromen-2-ylidene complexes **5** (Scheme 2).

The structural assignment of pyran-2-ylidene complexes **3** and **5** is based on spectroscopic data and on X-ray structure analyses of compounds **3b**[8] and **5c** (Figure 1, Tables 1−3). Compounds **3** and **5** are considered resonance hybrides between pyran-2-ylidene and pyrylium ylide structures. The pyrylium character of compound **5c** is indicated by the pattern of (essentially) non-alternating bond distances between the ring atoms [C(1)−O 1.382(11) Å, C(1)−C(2) 1.410(12), C(2)−C(3) 1.391(12), C(3)−C(4) 1.430(12), C(4)−C(13) 1.381(12), C(13)−O 1.343(11)] and is similar to that found for pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (**3b**).[8] Furthermore, the distance W−C1 2.182(9) Å proves to be significantly longer than the distance W═C, e.g., in $(CO)_5W{=}C(OMe)Ph$ (2.05 Å).[17] Further indication of the pyrylium character of **5c** is based upon the strong deshielding of NMR signals of C13 (δ 178.8)[18] and 2H (δ 8.04) and a significant upfield shift of C1 (δ 250.6) compared to the shift of the carbene carbon atom of $(CO)_5W{=}C(OEt)Ph$ (δ 319.6).[19]

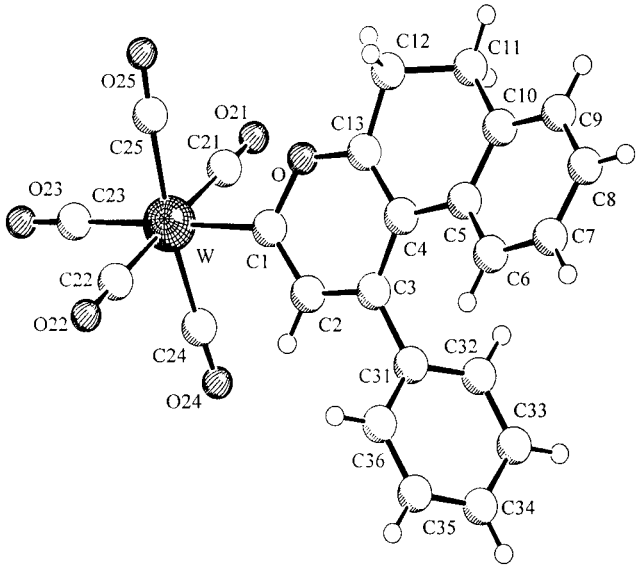


Figure 1. Molecular structure of pyran-2-ylidene complex **5c**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **5c**

W−C(1)	2.182(9)	C(5)−C(10)	1.423(12)
C(1)−O	1.382(11)	C(6)−C(7)	1.371(13)
C(1)−C(2)	1.410(12)	C(7)−C(8)	1.375(15)
C(2)−C(3)	1.391(12)	C(8)−C(9)	1.386(15)
C(3)−C(4)	1.430(12)	C(9)−C(10)	1.358(13)
C(3)−C(31)	1.464(12)	C(10)−C(11)	1.516(13)
C(4)−C(13)	1.381(12)	C(11)−C(12)	1.534(14)
C(4)−C(5)	1.465(12)	C(12)−C(13)	1.482(12)
C(5)−C(6)	1.401(12)	C(13)−O	1.343(11)
C(23)−W−C(1)	177.6(4)	C(6)−C(5)−C(4)	123.4(8)
C(22)−W−C(1)	90.3(3)	C(10)−C(5)−C(4)	119.2(8)
C(25)−W−C(1)	89.0(3)	C(7)−C(6)−C(5)	121.2(9)
C(24)−W−C(1)	87.7(3)	C(6)−C(7)−C(8)	121.3(9)
C(21)−W−C(1)	89.5(3)	C(7)−C(8)−C(9)	117.0
O−C(1)−C(2)	113.2(7)	C(10)−C(9)−C(8)	122.8(9)
O−C(1)−W	117.7(6)	C(9)−C(10)−C(5)	119.5(9)
C(2)−C(1)−W	129.1(6)	C(9)−C(10)−C(11)	121.9(8)
C(3)−C(2)−C(1)	124.8(8)	C(5)−C(10)−C(11)	118.6(8)
C(2)−C(3)−C(4)	118.0(8)	C(10)−C(11)−C(12)	109.1(8)
C(2)−C(3)−C(31)	117.8(7)	C(13)−C(12)−C(11)	109.7(8)
C(4)−C(3)−C(31)	124.3(8)	O−C(13)−C(4)	122.8(8)
C(13)−C(4)−C(3)	116.5(8)	O−C(13)−C(12)	114.8(8)
C(13)−C(4)−C(5)	117.0(8)	C(4)−C(13)−C(12)	122.4(8)
C(3)−C(4)−C(5)	126.4(8)	C(13)−O−C(1)	124.4(7)
C(6)−C(5)−C(10)	117.3(8)		

1,3-Cyclohexadiene Annulation to 1-Aminocyclopentenes and Formation of Steroid-Like Molecules. Addition of an enamine (**6**, **9**, or **13**) to a pyran-2-ylidene complex (**3** or **5**) in a hydrocarbon solvent leads to the formation of a cyclohexadiene annulation product, which is accumulated in solution, while

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Table 2. Details of X-ray Crystal Structure Analyses for **8b** and **5c**

formula	$C_{28}H_{31}NO$	$C_{24}H_{14}O_6W$
a (Å)	8.987(1)	9.188(1)
b (Å)	9.876(1)	12.244(4)
c (Å)	13.434(1)	12.707(2)
α (deg)	81.39(1)	63.23(2)
β (deg)	75.84(1)	72.61(1)
γ (deg)	71.32(1)	69.03(2)
vol (Å^3)	1091.9(2)	1175.4(4)
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius MACH III
data coll temp (K)	223	223
λ (Å)	1.54178	0.71073
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Z	2	2
μ (cm^{-1})	5.52	49.55
empirical abs corr	94.6−99.9%	83.8−99.8%
θ_{max} (deg)	74.28	26.28
no. of data collected	4750	4992
no. of unique data	4452	4769
R_{merge}	0.030	0.076
no. of data obsd ($\geq 2\sigma(I)$)	3941	3878
no. of refined params	273	290
R1 [$\geq 2\sigma$(I)]	0.046	0.055
wR2 [$\geq 2\sigma$(I)]	0.127	0.139
Flack param		
goodness of fit	1.028	1.027
programs used	MolEN, SHELXS-86 and SHELXL-93	

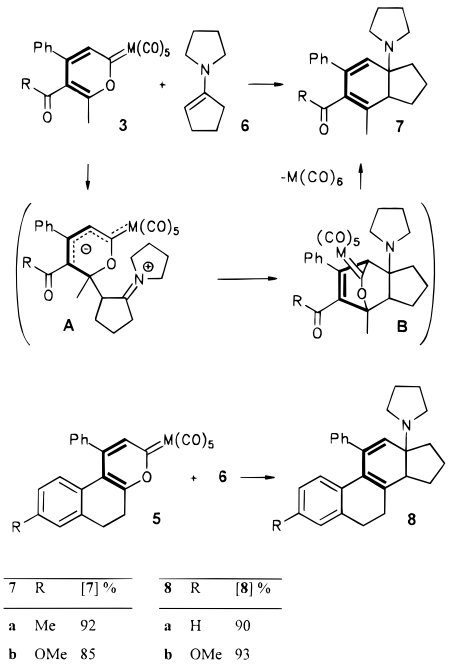
Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for **5c**[a]

	x	*y*	*z*	*U*(eq)
W	0.1391(1)	0.2309(1)	0.4223(1)	0.028(1)
C(21)	−0.0984(12)	0.2675(9)	0.4250(8)	0.034(2)
O(21)	−0.2273(9)	0.2885(9)	0.4251(8)	0.058(2)
C(22)	0.3757(13)	0.1900(10)	0.4226(10)	0.043(2)
O(22)	0.5064(10)	0.1647(11)	0.4255(10)	0.078(3)
C(23)	0.0999(12)	0.3177(9)	0.5342(9)	0.036(2)
O(23)	0.0762(10)	0.3638(8)	0.6012(7)	0.052(2)
C(24)	0.1246(10)	0.0608(9)	0.5606(8)	0.030(2)
O(24)	0.1146(9)	−0.0321(7)	0.6341(6)	0.046(2)
C(25)	0.1330(14)	0.3996(10)	0.2779(9)	0.043(2)
O(25)	0.1167(14)	0.4938(8)	0.2008(8)	0.069(3)
C(1)	0.1919(11)	0.1359(8)	0.3003(8)	0.033(2)
C(2)	0.2699(11)	0.0084(8)	0.3172(8)	0.028(2)
C(3)	0.2889(10)	−0.0456(8)	0.2367(8)	0.028(2)
C(4)	0.2410(10)	0.0363(8)	0.1230(8)	0.027(2)
C(5)	0.2687(10)	0.0016(8)	0.0209(8)	0.028(2)
C(6)	0.3929(10)	−0.0988(9)	0.0027(8)	0.032(2)
C(7)	0.4141(12)	−0.1273(10)	−0.0945(9)	0.041(2)
C(8)	0.3174(13)	−0.0558(11)	−0.1796(9)	0.043(2)
C(9)	0.1954(13)	0.0447(10)	−0.1630(9)	0.040(2)
C(10)	0.1700(11)	0.0762(9)	−0.0681(8)	0.031(2)
C(11)	0.0406(13)	0.1901(9)	−0.0545(9)	0.043(2)
C(12)	0.1016(14)	0.2548(9)	−0.0037(9)	0.042(2)
C(13)	0.1634(11)	0.1607(9)	0.1076(8)	0.032(2)
C(31)	0.3528(10)	−0.1832(9)	0.2751(8)	0.029(2)
C(32)	0.2664(11)	−0.2557(9)	0.2762(8)	0.033(2)
C(33)	0.3209(13)	−0.3845(10)	0.3158(10)	0.043(2)
C(34)	0.4754(15)	−0.4444(9)	0.3505(11)	0.051(3)
C(35)	0.5600(14)	−0.3714(10)	0.3452(11)	0.053(3)
C(36)	0.5046(11)	−0.2423(10)	0.3068(9)	0.040(2)
O	0.1412(8)	0.2065(6)	0.1910(6)	0.033(1)
C(40)	0.4992(19)	0.5083(30)	−0.0625(12)	0.198(8)
C(41)	0.3427(31)	0.5928(20)	−0.1028(26)	0.198(8)
C(42)	0.2490(29)	0.5140(29)	−0.1045(29)	0.198(8)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

$M(CO)_6$ is precipitated from the reaction mixture (Scheme 3). Reaction of 1-aminocyclopentene **6** proceeds faster (5−30 min at 20 °C) than that of 1-aminocyclohexene **9** (5−20 h at 20 °C) and much faster than that of 1-aminocycloheptene **13** (ca. 18 h at 90 °C). Furthermore, a pyran-2-ylidene complex **3**, which is activated by an electron-withdrawing acetyl group at C5, is more reactive toward the addition of an enamine than a benzo[*d*]chromen-2-ylidene complex **5**. An explanation of the reaction course of the cyclohexadiene annulation is based on the fact that the addition of primary amines to pyran-2-ylidene (pyrylium ylide) complex **3b** was shown to result in initial formation of a zwitterionic adduct to C6 of the pyran-2-ylidene ring.[8] Hence, addition of an enamine **6** to compound **3** is expected to afford a zwitterionic species **A**, which provides for an optimal delocalization of negative charge. It is assumed that a bicyclo[4.3.0]heptadiene **7** is obtained from **A** by retrocycloaddition of $M(CO)_6$ (M = Cr, W) (Scheme 3). The marked influence of the enamine ring size on the reaction rate is in line with an assumption that a six-membered intermediate **B** is formed in the rate-determining step.

Scheme 3. Condensation of Pyran-2-ylidene Complexes with 1-Aminocyclopentene **6**



7	R	[7] %	8	R	[8] %
a	Me	92	a	H	90
b	OMe	85	b	OMe	93

The elegance of the cyclohexadiene annulation via pyran-2-ylidene complexes is demonstrated by the generation of amino steroid-like ring skeletons,[20] e.g., compound **8**, in high chemical yields simply by the addition of an enamine **6** to a benzo[*d*]-chromen-2-ylidene complex **5**. Although compounds **7** and **8** contain a 1-aminocyclo-2,4-hexadiene unit, they are quite stable under ambient conditions and can be isolated by chromatography on silica gel without decomposition. Elimination of pyrrolidine is slow, probably due to an unfavorable transition state configuration resulting from the non-planar cis arrangement of the C−N and the C−H bond in the (distorted and essentially rigid) five-membered ring system. From the X-ray analysis of **8b** (Figure 2, Tables 2, 4, and 5) the dihedral angle N−C13−C14−14H was determined to be −34.7°.[18] The pyrrolidine moiety of **8a**,**b** was found to be thermally eliminated when subjected to GC−MS studies at 200 °C.

1,3-Cyclohexadiene Annulation to 1-Aminocyclohexenes. Reaction of pyran-2-ylidene complexes **3** with 1-aminocyclohexene **9** results in the formation of a hexahydronaphthalene **10**, while benzo[*d*]chromen-2-ylidene complexes **5** afford an aminooctahydrochrysene **11** (Scheme 4). Compounds **10** and **11** are stable in C_6D_6 at 70 °C for at least for 3 days with the cyclohexadiene annulation to the six-membered ring enamine **9** being slower than to the five-membered ring enamine **6**. However, and in contrast, cis elimination of pyrrolidine from

(20) Pancrazi, A.; Khuong-Huu, Q. *Tetrahedron* **1974**, *30*, 2337−2343.

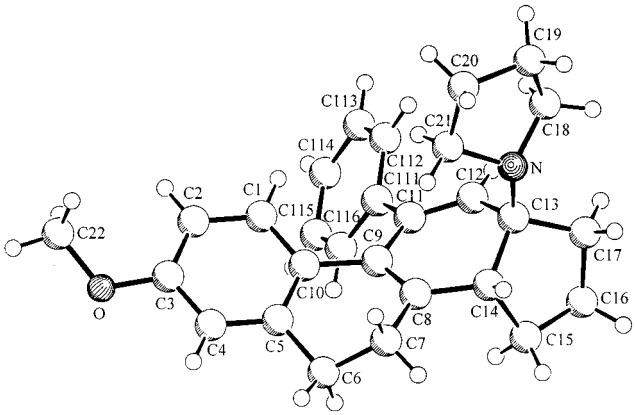


Figure 2. Molecular structure of amino steroid **8b**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **8b**

C(1)−C(10)	1.397(2)	C(11)−C(111)	1.493(2)
C(2)−C(3)	1.385(2)	C(12)−C(13)	1.512(2)
C(3)−O	1.374(2)	C(13)−N	1.482(2)
C(3)−C(4)	1.392(2)	C(13)−C(14)	1.541(2)
C(4)−C(5)	1.379(2)	C(13)−C(17)	1.543(2)
C(5)−C(10)	1.411(2)	C(14)−C(15)	1.552(2)
C(5)−C(6)	1.505(2)	C(15)−C(16)	1.504(3)
C(6)−C(7)	1.519(2)	C(16)−C(17)	1.524(3)
C(7)−C(8)	1.506(2)	N−C(18)	1.466(2)
C(8)−C(9)	1.355(2)	N−C(21)	1.467(2)
C(8)−C(14)	1.496(2)	C(18)−C(19)	1.519(3)
C(9)−C(10)	1.483(2)	C(19)−C(20)	1.533(3)
C(9)−C(11)	1.488(2)	C(20)−C(21)	1.530(2)
C(11)−C(12)	1.342(2)	O−C(22)	1.410(2)
C(2)−C(1)−C(10)	121.95(12)	C(9)−C(11)−C(111)	121.34(11)
C(3)−C(2)−C(1)	119.24(12)	C(11)−C(12)−C(13)	123.89(12)
O−C(3)−C(2)	124.80(13)	N−C(13)−C(12)	112.91(11)
O−C(3)−C(4)	115.38(12)	N−C(13)−C(14)	111.49(10)
C(2)−C(3)−C(4)	119.80(12)	C(12)−C(13)−C(14)	108.75(11)
C(5)−C(4)−C(3)	120.96(12)	N−C(13)−C(17)	110.26(11)
C(4)−C(5)−C(10)	120.36(12)	C(12)−C(13)−C(17)	110.60(11)
C(4)−C(5)−C(6)	120.98(12)	C(14)−C(13)−C(17)	102.33(12)
C(10)−C(5)−C(6)	118.66(12)	C(8)−C(14)−C(13)	114.74(11)
C(5)−C(6)−C(7)	109.80(11)	C(8)−C(14)−C(15)	112.57(12)
C(8)−C(7)−C(6)	110.78(11)	C(13)−C(14)−C(15)	105.61(11)
C(9)−C(8)−C(14)	121.73(12)	C(16)−C(15)−C(14)	106.69(14)
C(9)−C(8)−C(7)	121.07(12)	C(15)−C(16)−C(17)	106.92(14)
C(14)−C(8)−C(7)	117.19(11)	C(16)−C(17)−C(13)	104.80(13)
C(8)−C(9)−C(10)	118.70(11)	C(18)−N−C(21)	103.48(12)
C(8)−C(9)−C(11)	118.22(11)	C(18)−N−C(13)	115.45(11)
C(10)−C(9)−C(11)	122.91(11)	C(21)−N−C(13)	116.69(11)
C(1)−C(10)−C(5)	117.66(12)	N−C(18)−C(19)	103.30(13)
C(1)−C(10)−C(9)	123.75(11)	C(18)−C(19)−C(20)	104.49(13)
C(5)−C(10)−C(9)	118.45(11)	C(21)−C(20)−C(19)	104.69(13)
C(12)−C(11)−C(9)	119.67(12)	N−C(21)−C(20)	103.63(12)
C(12)−C(11)−C(111)	118.70(11)	C(3)−O−C(22)	117.52(12)

11 on contact with silica gel to afford an aromatic compound **12** proceeds faster than with **8** (Scheme 3).

1,3-Cyclohexadiene Annulation to 1-Aminocycloheptenes. The reaction of 1-amino cycloheptene **13** with benzo[*d*]chromen-2-ylidene complex **5a** is sluggish and requires heating to 90 °C (Scheme 5). Although a singulet at δ 5.78 was observed in the ^{1}H NMR spectrum of the crude reaction mixture, which indicated that the cyclohexadiene annulation product **14** had been formed, this could not be isolated by chromatography since it readily underwent aromatization on silica gel to give compound **15** by elimination of morpholine.

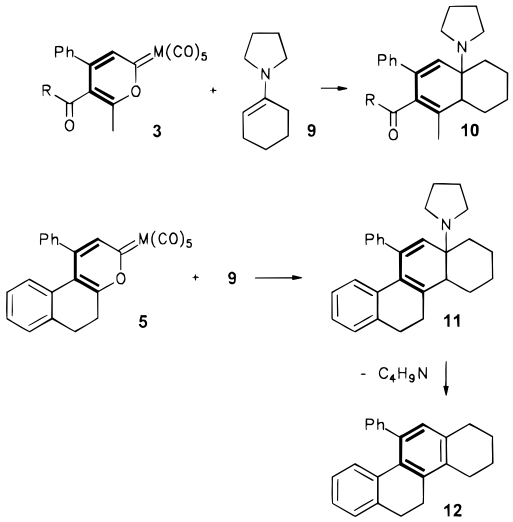
Alternate Route to Steroid−Like Ring Skeletons. A further approach to the formation of steroid-like ring skeletons via the cyclohexadiene annulation procedure, which is complementary to that shown in Scheme 3, is achieved by condensation of a cyclopentano pyran-2-ylidene complex **17**[9] with 1-amino-

Table 5. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for **8b**[a]

	x	*y*	*z*	*U*(eq)
C(1)	0.7408(2)	−0.2608(1)	0.2600(1)	0.033(1)
C(2)	0.6556(2)	−0.1157(2)	0.2535(1)	0.037(1)
C(3)	0.5775(2)	−0.0600(1)	0.1727(1)	0.038(1)
C(4)	0.5832(2)	−0.1495(2)	0.1002(1)	0.039(1)
C(5)	0.6682(2)	−0.2930(1)	0.1064(1)	0.033(1)
C(6)	0.6737(2)	−0.3900(2)	0.0283(1)	0.039(1)
C(7)	0.6631(2)	−0.5346(1)	0.0815(1)	0.036(1)
C(8)	0.7866(2)	−0.5951(1)	0.1473(1)	0.031(1)
C(9)	0.8353(1)	−0.5080(1)	0.1928(1)	0.030(1)
C(10)	0.7514(1)	−0.3519(1)	0.1867(1)	0.030(1)
C(11)	0.9622(1)	−0.5748(1)	0.2535(1)	0.031(1)
C(12)	0.9943(2)	−0.7147(1)	0.2852(1)	0.036(1)
C(13)	0.9082(2)	−0.8121(1)	0.2631(1)	0.035(1)
C(14)	0.8504(2)	−0.7548(1)	0.1617(1)	0.035(1)
C(15)	0.9955(2)	−0.8182(2)	0.0746(1)	0.052(1)
C(16)	1.1118(2)	−0.9379(2)	0.1249(2)	0.070(1)
C(17)	1.0277(2)	−0.9603(2)	0.2366(1)	0.048(1)
N	0.7740(1)	−0.8287(1)	0.3487(1)	0.037(1)
C(18)	0.8208(2)	−0.9035(2)	0.4441(1)	0.054(1)
C(19)	0.6608(2)	−0.8882(2)	0.5194(1)	0.059(1)
C(20)	0.5487(2)	−0.7474(2)	0.4815(1)	0.053(1)
C(21)	0.6504(2)	−0.6965(2)	0.3830(1)	0.039(1)
O	0.4935(2)	0.0816(1)	0.1562(1)	0.056(1)
C(22)	0.4407(2)	0.1670(2)	0.2406(1)	0.044(1)
C(111)	1.0666(1)	−0.4935(1)	0.2711(1)	0.032(1)
C(112)	1.1178(2)	−0.5138(2)	0.3635(1)	0.042(1)
C(113)	1.2265(2)	−0.4472(2)	0.3757(1)	0.052(1)
C(114)	1.2856(2)	−0.3602(2)	0.2963(2)	0.052(1)
C(115)	1.2338(2)	−0.3377(2)	0.2050(1)	0.044(1)
C(116)	1.1243(2)	−0.4023(1)	0.1926(1)	0.035(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Scheme 4. Condensation of Pyran-2-ylidene Complexes with 1-Aminocyclohexene **9** (M = Cr, W)

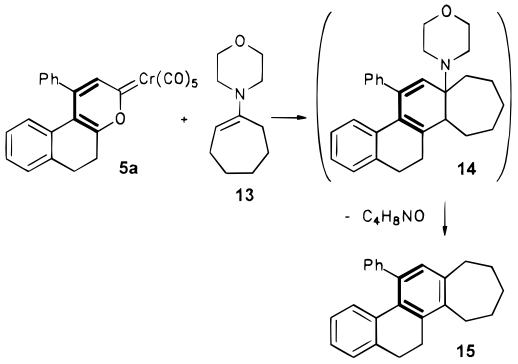


10	R	[**10**] %	**11** (90 %)
a	Me	87	**12** (0 - 90 %)
b	OMe	95	

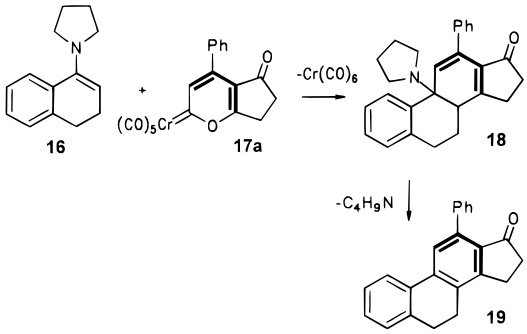
dehydronaphthalene **16** (Scheme 6). Compounds **17a**,**b** are obtained by condensation of 1,3-cyclopentandione with alkynylcarbene complexes **1a**,**b** with the subsequent formation of the steroid-like ring skeleton **18** proceeding in a smooth reaction. These compounds prove to be quite stable in solution at ambient temperature, but elimination of pyrrolidine to give compound **19** occurs rapidly if isolation is attempted by chromatography on silica gel.

1,3-Cyclohexadiene Annulation to Enoles. The 1,3-cyclohexadiene annulation to enamines can be extended also to

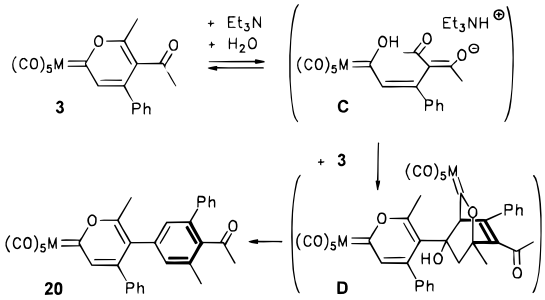
Scheme 5. Condensation of Pyran-2-ylidene Complexes with 1-Aminocycloheptene **13**



Scheme 6. Alternate Route to Steroid-Like Compounds



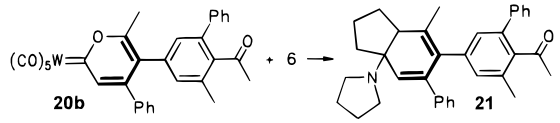
Scheme 7. Base-Induced Self-Condensation of Pyran-2-ylidene Complexes



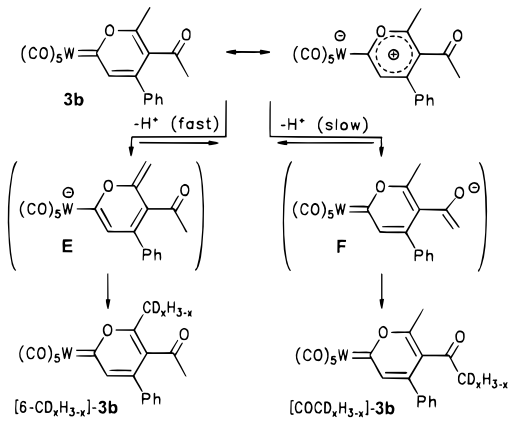
enoles. An interesting application of a 1,3-cyclohexadiene annulation to an enol is represented by the base-induced self-condensation of pyran-2-ylidene complexes **3** (Scheme 7). This latter process must be noted in the context of our present studies, since it may (unwantedly) even become the main reaction if generation of pyran-2-ylidene complexes is attempted in polar solvents, like THF or acetone. As has been mentioned above, base-induced condensation of ketones with alkynylcarbene complexes **1a,b** (Scheme 2) usually provides high chemical yields of pyran-2-ylidene complexes **3**. Importantly, this transformation must be carried out under carefully controlled reaction conditions in pentane since the product complexes are only sparingly soluble in this solvent.[8] However, if the same processes are undertaken in homogeneous solution, two side reactions may cause a severe drop in chemical yield. These are (a) the base-induced self-condensation of a pyran-2-ylidene complex **3** (Scheme 7) and (b) the possible base-induced condensation of a pyran-2-ylidene complex **3** with the carbonyl component (Scheme 10). We herein wish to present examples of these possible side reactions.

Self-Condensation of Pyran-2-ylidene Complexes. Pyran-2-ylidene complexes **3a,b** are not stable in solution in presence of a base and readily undergo self-condensation to form (cherry-red) biphenyl derivatives **20a,b** (Scheme 7). Compounds **20a,b**

Scheme 8. Enaminolysis of Pyran-2-ylidene Complex **20b**



Scheme 9. H/D Exchange in Pyran-2-ylidene Complex **3b**

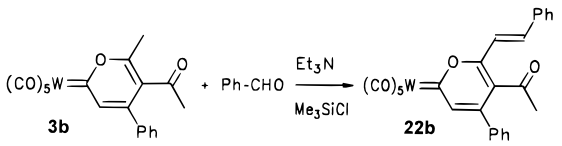


are obtained in up to 82−85% yields, if pyran-2-ylidene complexes **3** are treated with Et_3N in acetone as solvent. These compounds are also generated in good yield if an ether solution of a pyran-2-ylidene complex **3a,b** is treated with aqueous NaOH in presence of $[Et_3N\text{-}CH_2Ph]Br$ as a PT catalyst. In this case, brick-red colored crystals separate and accumulate in the ether phase together with $M(CO)_6$. However, formation of **20** can be strongly retarded if pyran-2-ylidene complexes **3** are prepared from **1** and **2** (Scheme 2) in a *hydrocarbon solvent*, in which they dissolve only sparingly. Since pyran-2-ylidene complexes **3** are precipitated under these conditions, they become sufficiently protected from undergoing self-condensation to give **20**. The reaction path leading to generation of **20** (Scheme 7) is based on our experience from studies of the aminolysis of **3**.[8] Accordingly, it is assumed that addition of H_2O and Et_3N to compound **3** leads to a (reversible) ring opening with the formation of an enolate **C**. Addition of **C** to a further molecule of pyran-2-ylidene complex **3** would then afford compound **20** via retrocycloaddition of $M(CO)_6$ from an intermediate **D**.

The structure of **20** is based upon spectroscopic evidence as well as on the reactivity of **20** toward enamine **6**. Addition of **6** to the tungsten complex **20b** affords the cyclohexadiene annulation compound **21** as the only detectable organic product (Scheme 8).

In context with our investigation of the base-induced self-condensation of complexes **3**, which we assume is initiated by nucleophilic attack of OH^- at C6 of the pyran-2-ylidene ring and subsequent ring opening to an intermediate **C** (Scheme 7), we have envisaged deprotonation of **3** as an alternate route to the formation of **20**. It can be demonstrated by ^1H NMR experiments that both methyl groups of compound **3b** undergo H/D exchange in $[D_6]$acetone in presence of Et_3N, which is faster than the self-condensation mentioned above (completed within 15 h at 20 °C) (Scheme 9). Furthermore, it can be deduced from ^1H NMR spectra taken continuously that incorporation of a deuterium atom into the 6-CH_3 (δ 2.67) group is ca. two times faster than incorporation into the CO-CH_3 (δ 1.92) group. This is to be expected since the negative charge is better stabilized by delocalization through the conjugated π system in anion **E** than in **F**. Although it cannot be fully excluded that it is the enolate anion **F** that adds to **3** in the first step of the self-condensation reaction, it appears to us that this reaction

Scheme 10. Condensation of Pyran-2-ylidene Complexes **3** with Benzaldehyde



path might be unfavorable for steric reasons. Furthermore, it could be suggested that in the case of pyran-2-ylidene complex **3b** the 6-CH_3 group would be more prone to undergo condensation reactions than the $COCH_3$ group.

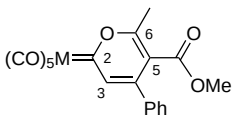
Thus, condensation of the pyran-2-ylidene complex **3b** with benzaldehyde in presence of Et_3N/Me_3SiCl affords product **22b** (Scheme 10). Proof for the structure of compound **22b** is based on the signals C6 at δ 168.2 (**3b**: 173.9), 6-*C*OCH_3 δ 199.3 (**3b**: 204.5), 6-CO*C*H_3 δ 31.7 (**3b**: 31.3) in the ^{13}C NMR spectrum as well as on the [ν(C═O)] band at 1699.0 cm^{-1} (**3b**: 1702.4) in the IR spectrum which, as shown, are similar to those of **3b**. It is worth noting that had the condensation of benzaldehyde occurred with the $COCH_3$ group, the spectroscopic values above would have been considerably different.

Experimental Section

All operations were carried out under an atmosphere of argon. Solvents were dried and distilled prior to use. ^1H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra were recorded on a Bruker ARX 300 instrument. ^{13}C NMR multiplicities were determined by DEPT, NOE, and DR spin-decoupling. IR spectra were recorded on a Biorad Digilab Division FTS-45 FT-IR spectrophotometer. GC/IR spectra were taken on a Shimadzu gas chromatograph GC-14A coupled to a Biorad Digilab Division GC/C32. 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), by exposure to iodine vapor or were stained by a 5% aqueous acidic ammonium molybdate solution. R_f values refer to TLC tests. Chromatographic purifications were performed on Merck Kieselgel 100.

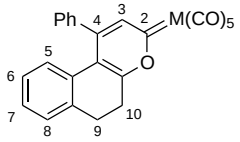
Pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)chromium (3a). To pentacarbonyl(1-ethoxy-3-phenyl-2-propyne-1-ylidene)chromium (**1a**) (350 mg, 1.00 mmol) in a 5-mL screwtop vessel is added a solution of pentane-2,4-dione **2** (100 mg, 1.00 mmol) and triethylamine (50 mg, 0.50 mmol) in 4 mL of pentane with efficient stirring at 20 °C until a dark (homogeneous) solution is obtained (after 3−5 min), from which violet crystals of **3a** begin to precipitate within 10 min at 20 °C. After 2 h at 20 °C, crystallization is continued at −15 °C for 12 h to give (additional) compound **3a** (368 mg, 91%, R_f = 0.5 pentane/dichloromethane 4:1, violet needles from diethyl ether). ^1H NMR (C_6D_6): δ 8.00 (1 H, s, 3-H), 6.90 (5 H, m, Ph), 1.90 (3 H, s, 6-CH_3), 1.29 (3 H, s, $OCCH_3$). ^{13}C NMR (C_6D_6): δ 283.4 (Cr═C), 224.7 and 118.6 [*trans*- and *cis*-CO, $Cr(CO)_5$], 199.4 (Cq, C═O), 175.9 (Cq, C6), 140.9 (Cq, C4), 139.3 (CH, C3), 135.7 (Cq, *i*-C, Ph); 131.4, 130.0, and 128.5 (CH each, Ph), 127.6 (Cq, C5), 31.3 (6-CH_3), 19.3 ($OCCH_3$). IR (diffusion reflection), cm^{-1}: 2052.9, 1979.7, 1915.5 [ν(C≡O)], 1701.4 [ν(C═O)]; IR (hexane): 2055.4 (30), 1983.1 (5), 1939.2 (100) [ν(C≡O)]. MS (70 eV), *m/e* (%): 404 (20) [M^+], 376 (10), 348 (20), 320 (20), 292 (30), 264 (50) [$M^+ - 5CO$], 52 (100). Anal. Calcd for $C_{19}H_{12}CrO_7$ (404.3): C, 56.45; H, 2.99. Found: C, 56.39; H, 2.76.

Pentacarbonyl(5-carbomethoxy-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (3c). To pentacarbonyl(1-ethoxy-3-phenyl-2-propyne-



1-ylidene)tungsten (**1b**) (482 mg, 1.00 mmol) in a 5-mL screwtop vessel is added a solution of methyl 3-oxobutyric acid methyl ester (**2b**) (100 mg, 1.00 mmol) and triethylamine (50 mg, 0.50 mmol) in 4 mL of pentane with efficient stirring at 20 °C until a dark (homogeneous) solution is obtained (after 3−5 min), from which violet crystals of **3c** begin to precipitate within 10 min at 20 °C. After 2 h at 20 °C, crystallization is continued at −15 °C for 12 h to give (additional) compound **3c** (480 mg, 87%, R_f = 0.5 diethyl ether/pentane 1:1). ^1H NMR ($CDCl_3$): δ 8.05 (1 H, s, 3-H), 7.50 (3 H, m, *p*- and *m*-H, Ph), 7.37 (2 H, m, *o*-H, Ph), 3.62 (3 H, s, CO_2CH_3), 2.67 (3 H, s, 6-CH_3). ^{13}C NMR ($CDCl_3$): δ 258.7 (W═C), 204.3 und 198.3 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 175.3 (Cq, C6), 165.6 (Cq, *C*O_2CH_3), 143.9 (Cq, C4), 141.4 (CH, C3), 135.7 (Cq, *i*-C, Ph); 130.6, 129.1, and 127.3 (CH each, Ph), 120.3 (Cq, C5), 53.0 (CO_2CH_3), 19.9 ($COCH_3$). IR (diffuse reflection), cm^{-1}: 2062.1, 1973.7, 1902.6 [ν(C≡O)], 1725.6 [ν(C═O)], 1599.3. MS (70 eV) *m/z* (%): 552 [M^+] (20), 412 [$M^+ - 5CO$] (20), 228 [ligand$^+$] (20), 165 (100). HRMS for $C_{19}H_{12}O_8W$ (552.2): *m/e* 549.99955 (calcd. 550.00147).

Pentacarbonyl(4-phenyl-9,10-dihydro-2*H*-benzo[*d*]chromen-2-ylidene)chromium (5a). To pentacarbonyl(1-ethoxy-3-phenyl-2-pro-



pyn-1-ylidene)chromium (**1a**) (385 mg, 1.10 mmol) in 4 mL of dry dichloromethane in a 5-mL screwtop vessel is added 2-tetralone (**4a**) (146 mg, 1.00 mmol) and triethylamine (50 mg, 0.50 mmol). According to TLC (pentane/dichloromethane 6:1) after 30 min at 20 °C, the reaction is approximately 50% completed. Solvent is removed after 4 h at 20 °C by passing a stream of argon through the solution. The residue is dissolved in 2 mL of toluene and separated by chromatography (column 15 × 2 cm) on silica gel. Elution with pentane/dichloromethane (4:1) affords a violet fraction of **5a** (422 mg, 88 %, R_f = 0.5 diethyl ether/pentane 1:6, red-brown crystals from dichloromethane/pentane 1:10, mp 144 °C). ^1H NMR (C_6D_6): δ 8.31 (1 H, s, 3-H), 7.07 (5 H, m, 4-Ph), 7.03 (1 H, t, 6-H), 7.00 (1 H, d, 5-H), 6.82 (1 H, t, 7-H), 6.72 (1 H, d, 8-H), 2.55 (2 H, t, 9-H_2), 2.44 (2 H, t, 10-H_2). ^{13}C NMR (C_6D_6): δ 276.5 (Cr═C), 224.1 and 218.6 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 179.7 (Cq, C10a), 142.1 (Cq, C4), 141.4 (CH, C3); 136.9, 135.5, and 130.1 (Cq each, *i*-C Ph, C4b, C8a); 130.4, 128.8, 128.5, and 126.5 (CH each, C5−C8); 129.5, 129.0, and 128.5 (2:2:1, CH each, Ph), 120.3 (Cq, C4a), 28.3 and 27.1 (CH_2 each, C9 and C10). IR (hexane), cm^{-1} (%): 2052.8 (30), 1977.9 (5), 1941.0 (100). MS (70 eV), *m/e* (%): 450 (20) [M^+], 422 (10), 394 (10), 366 (20), 338 (20), 310 (100) [$M^+ - 5CO$]. Anal. Calcd for $C_{24}H_{14}CrO_6$ (450.4): C, 64.01; H, 3.13. Found: C, 64.22; H, 3.40.

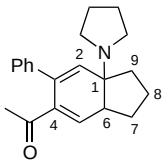
Pentacarbonyl(7-methoxy-4-phenyl-9,10-dihydro-2*H*-benzo[*d*]-chromen-2-ylidene)chromium (5b). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)chromium (**1a**) (385 mg, 1.10 mmol) is reacted as described above with 6-methoxy-2-tetralone (**4b**) (176 mg, 1.00 mmol) for 12−20 h at 20 °C to give **5b** (365 mg, 76 %, R_f = 0.5 pentane/dichloromethane 4:1, violet crystals from dichloromethane/pentane 1:10). ^1H NMR (C_6D_6): δ 8.08 (1 H, s, 3-H), 7.05 (5 H, m, 4-Ph), 6.42 (1 H, d, ^4J = 2.5 Hz, 8-H), 6.38 (1 H, d, ^3J = 9 Hz, 5-H), 6.08 (1 H, dd, ^4J = 2.5 Hz, ^3J = 9, 6-H), 3.10 (3 H, s, OCH_3), 2.32 (2 H, t, 9-H_2), 2.13 (2 H, t, 10-H_2). ^{13}C NMR (C_6D_6): δ 273.6 (Cr═C), 224.3, and 218.7 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 179.2 (Cq, C10a), 159.8 (Cq, C7), 142.3 (Cq, C4), 141.3 (CH, C3); 137.4 and 137.2 (Cq each, *i*-C Ph and C8a), 121.1 and 120.7 (Cq each, C4a and C4b); 130.0 (CH, C5); 129.9, 129.2, and 128.6 (2:2:1, CH each, Ph); 114.1 and 111.4 (CH each, C6 and C8), 54.8 (OCH_3), 28.4 and 27.5 (CH_2 each, C9 and C10). IR (hexane), cm^{-1} (%): 2052.8 (30), 1975.5 (5), 1935.8 (100). MS (70 eV), *m/e* (%): 481 (30) [$M^+ + 1$], 480 (30) [M^+], 452 (10), 424 (15), 396 (20), 368 (20), 340 (40), 288 (40) [ligand$^+$], 52 (100). Anal. Calcd for $C_{25}H_{16}CrO_7$ (480.4): C, 62.51; H, 3.36. Found: C, 62.31; H, 3.30.

Pentacarbonyl(4-phenyl-9,10-dihydro-2*H*-benzo[*d*]chromen-2-ylidene)tungsten (5c). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1b**) (530 mg, 1.10 mmol) is reacted as described above with 2-tetralone (**4a**) (146 mg, 1.00 mmol) for 12−20 h at 20 °C to give **5c** (372 mg, 64 %, R_f = 0.5 pentane/dichloromethane 4:1, red lustrous plates from dichloromethane/pentane (1:4) at −18 °C, mp

137−138 °C). ^{1}H NMR (C_6D_6): δ 8.04 (1 H, s, 3-H), 7.05 (1 H, m, 4-Ph), 6.94 (4 H, m, 4-Ph), 6.81 (1 H, t, 6-H), 6.76 (1 H, t, 5-H), 6.55 (1 H, t, 7-H), 6.47 (1 H, d, 8-H), 2.22 (4 H, m, 9-H_2 and 10-H_2). ^{13}C NMR (C_6D_6): δ 250.6 (W═C), 204.3 and 199.4 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 178.8 (Cq, C10a), 145.3 (Cq, C4), 143.6 (CH, C3); 136.9, 135.5, and 129.0 (Cq each, *i*-C Ph, C4b, C8a); 130.2, 127.7, 127.3, and 126.3 (CH each, C5−C8); 129.2, 128.4, and 128.1 (2:2:1, CH each, Ph); 121.1 (Cq, C4a), 28.4 and 27.0 (CH_2 each, C9 and C10). IR (hexane), cm^{-1} (%): 2060.3 (25), 1972.2 (5), 1940.4 (100). MS (70 eV), *m/e* (%): 582 (25) [M$^-$], 581 (15) [M$^+$ − 1], 554 (5), 526 (25), 498 (30), 470 (20), 442 (25) [M$^+$ − 5CO], 270 (90), 268 (100); HRMS (Ref = 592.96332) for $C_{24}H_{14}O_6W$: *m/e* 582.03216 (calcd. 582.02999).

Pentacarbonyl(7-methoxy-4-phenyl-9,10-dihydro-2*H*-benzo[*d*]-chromen-2-ylidene)tungsten (5d). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1b**) (530 mg, 1.10 mmol) is reacted as described above with 6-methoxy-2-tetralone (**4b**) (176 mg, 1.00 mmol) for 12−20 h at 20 °C to give **5d** (496 mg, 81%, R_f = 0.5 pentane/dichloromethane 4:1, red/violet lustrous plates and cubes from dichloromethane/pentane (1:4) at −78 °C, mp 141−142 °C). ^{1}H NMR (C_6D_6): δ 8.05 (1 H, s, 3-H), 7.04 (1 H, m, 4-Ph), 6.96 (4 H, m, 4-Ph), 6.41 (1 H, d, ^4J = 3.8 Hz, 8-H), 6.39 (1 H, d, ^3J = 8.8 Hz, 5-H), 6.07 (1 H, dd, ^4J = 2.9 Hz, ^3J = 8.8 Hz, 6-H), 3.16 (3 H, s, OMe), 2.23 (2 H, t, 9-H_2), 2.11 (2 H, t, 10-H_2). ^{13}C NMR (C_6D_6): δ 248.9 (W═C), 204.3 and 199.5 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 178.1 (Cq, C10a), 159.9 (Cq, C7), 145.1 (Cq, C4), 143.5 (CH, C3); 137.4 and 137.2 (Cq each, *i*-C Ph and C8a), 130.0 (CH, C5); 129.8, 129.2, and 128.4 (2:2:1, CH each, Ph), 121.4 and 121.2 (Cq each, C4a and C4b); 114.1 and 111.4 (CH each, C6 and C8), 54.8 (OCH_3), 28.5, and 27.4 (CH_2 each, C9 and C10). IR (hexane), cm^{-1} (%): 2059.9 (25), 1975.0 (5), 1936.5 (100). MS (70 eV), *m/e* (%): 613 (60) [M$^+$ + 1], 612 (60) [M$^+$], 556 (50), 528 (75), 500 (50), 472 (100) [M$^+$ − 5CO]; HRMS (Ref = 604.96332) for $C_{25}H_{16}O_7W$: *m/e* 612.04017 (calcd. 612.04102). Anal. Calcd for $C_{25}H_{16}O_7W$ (612.3): C, 49.04; H, 2.63. Found: C, 48.83; H, 2.64.

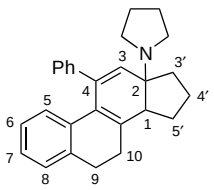
4-Acetyl-5-methyl-3-phenyl-1-pyrrolidinobicyclo[4.3.0]nona-2,4-diene (7a). To pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-



ylidene)tungsten (**3b**) (268 mg, 0.50 mmol) in 1 mL of C_6D_6, with hexamethylbenzene as an internal standard, is added 1-pyrrolidinocyclopentene (**6**) (68.5 mg, 0.50 mmol). The initially dark-red solution gradually becomes orange. According to TLC, the starting material is consumed completely after 30 min at 20 °C. The ^{1}H NMR spectrum of the solution indicates that compound **7a** has been formed as the only detectable product. Chromatography on silica gel with dichloromethane affords colorless $Cr(CO)_6$ and small amounts of colored products, which are discarded. Elution with acetone/water 10:1 gives colorless **7a** (295 mg, 92 %, R_f = 0.5 in acetone/water 10:1, detected on silica gel after exposure to iodine vapors, colorless crystals from diethyl ether/pentane at −15 °C). Similar results are obtained on reaction of pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)chromium (**3a**) (210 mg, 0.50 mmol) with 1-pyrrolidinocyclopentene (**6**) (68.5 mg, 0.50 mmol). ^{1}H NMR (C_6D_6): δ 7.29, 7.05, and 7.02 (2:1:2 H, Ph), 5.40 (1 H, s, 2-H), 2.60 and 1.59 (4:4 H, m each, pyrrolidine), 2.27 (1 H, dd, ^3J = 8.3 and 8.3 Hz, 6-H); 2.12 and 2.03 (1:1 H, m each, 7-H_2), 1.89 (3 H, s, $COCH_3$); 1.75, 1.45, and 1.35 (1:1:2, m each, 9-H_2 and 8-H_2), 1.68 (5-CH_3). ^{13}C NMR (C_6D_6): δ 203.3 (*C*OMe); 142.0, 141.8, 138.2, and 133.6 (Cq each, C3, C4, C5, and *i*-C Ph); 129.1, 127.9, 127.8, and 126.7 (2:1:2:1, CH each, C-2 and Ph), 63.8 (CH, C6), 51.1 (Cq, C1), 47.2, and 24.4 (2 CH_2 each, pyrrolidine); 42.1, 34.7, and 23.8 (CH_2 each, C7 − C9), 31.4 ($COCH_3$), 20.2 (5-CH_3). IR (diffuse reflection), cm^{-1}: 1690.7 [ν(C═O)]. MS (70 eV), *m/e* (%): 321 (5) [M$^+$], 306 (5), 278 (50) [M$^+$ − COMe], 250 (20), 235 (100) [M$^+$ − HNC_4H_8], 217 (20). Anal. Calcd for $C_{22}H_{27}NO$ (321.5): C, 82.20; H, 8.47; N, 4.36. Found: C, 82.42; H, 8.64; N, 4.53.

4-Carbomethoxy-5-methyl-3-phenyl-1-pyrrolidinobicyclo[4.3.0]-nona-2,4-diene (7b). Pentacarbonyl(5-carbomethoxy-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten[21] (**3c**) (274 mg, 0.50 mmol) in 1 mL of C_6D_6 is reacted as described above with 1-pyrrolidinocyclopentene (**6**) (68.5 mg, 0.50 mmol). The reaction is complete within 5 min at 20 °C and affords **7b** (143 mg, 85 %, R_f = 0.5 in acetone/water 10:1, detected on silica gel after exposure to iodine vapor, colorless crystals. ^{1}H NMR (C_6D_6): δ 7.40 and 7.18−7.05 (2:3 H, Ph), 5.47 (1 H, s, 2-H), 3.14 (3 H, s, OMe), 2.68 and 2.58 (2 H each, m each, NCH_2 each, pyrrolidine), 2.28 (1 H, dd, ^3J = 8.1 and 8.8 Hz, 6-H); 2.16−2.06 (2 H, m, 7-H_2), 2.02 (3 H, s, 5-CH_3), 1.79 and 1.56−1.36 (1:3, m each, 9-H_2 and 8-H_2), 1.60 (4 H, m, NCH_2-CH_2-CH_2, pyrrolidine). ^{13}C NMR (C_6D_6): δ 169.3 (CO_2Me); 145.4, 142.4, 138.7, and 125.1 (Cq each, C3, C4, C5, and *i*-C Ph); 128.4, 127.1, 127.0, and 125.4 (2:1:2:1, CH each, C-2 and Ph), 63.9 (Cq, C1), 51.0 (CH, C6), 50.7 (OCH_3), 46.9 and 24.0 (2 CH_2 each, pyrrolidine); 41.7, 34.1, and 23.6 (CH_2 each, C7−C9), 20.3 (5-CH_3). IR (diffuse reflection), cm^{-1}: 1719.6 [ν(C═O)]. MS (70 eV), *m/e* (%): 337 (20) [M$^+$], 322 (10) [M$^+$ − CH_3], 294 (10) [M$^+$ − CO_2Me], 278 (10), 266 (15), 235 (20), 149 (30), 86 (85), 84 (100); HRMS (Ref = 339.97927) for $C_{22}H_{27}NO_2$: *m/e* 337.20332 (calcd.337.20418).

4-Phenyl-2-pyrrolidino-1,2,9,10-tetrahydro-1,2-cyclopentanophenanthrene (8a). Pentacarbonyl(4-phenyl-9,10-dihydro-2*H*-benzo-

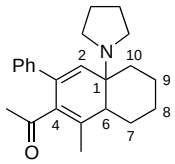


[*d*]chromen-2-ylidene)chromium (**5a**) (225 mg, 0.50 mmol) in 1 mL of C_6D_6 and hexamethylbenzene as an internal standard is reacted with 1-pyrrolidinocyclopentene (**6**) (68.5 mg, 0.50 mmol) as described above for 5 h at 20 °C. According to ^{1}H NMR spectra, compound **8a** is formed as the only detectable product. Chromatography gives colorless **8a** (330 mg, 90 %, R_f = 0.5 in acetone/water 10:1, detected on silica gel after exposure to iodine vapors, colorless crystals from dichloromethane/pentane 1:20 at −15 °C, mp 153 °C). Reaction of pentacarbonyl(4-phenyl-9,10-dihydro-2*H*-benzo[*d*]chromen-2-ylidene)-tungsten (**5c**) with **6** for 6 h at 20 °C affords **8a** in 99%. ^{1}H NMR (C_6D_6): δ 7.38 and 7.05 (2:3 H, Ph); 7.02, 6.88, 6.78, and 6.72 (1 H each, d, t, d, t, 5-H−8-H), 5.65 (1 H, s, 3-H); 2.80, 2.55, 2.15, and 2.10 (1 H each, m each, 9-H_2 and 10-H_2), 2.59 and 1.56 (4 H each, m each, pyrrolidine), 2.35 (1 H, dd, ^3J = 8.5 and 8.5 Hz, 1-H); 2.18 and 2.03 (1 H each, m each, 5′-H_2), 1.88, 1.64, and 1.48 (1:1:2 H, m each, 4′-H_2 and 3′-H_2). ^{13}C NMR (C_6D_6): δ 144.8, 142.8, 140.7, 136.6, 134.1, and 125.7 (Cq each, C4, C4a, C4b, 8a, 10a, and *i*-C Ph); 129.2, 128.7, and 128.3 (2:2:1, CH each, Ph); 127.6, 127.4, 127.2, 126.2, and 125.9 (1:1:1:1:1, CH each, C5−C8 and C3), 63.4 (Cq, C2), 50.4 (CH, C1), 47.3 and 23.9 (2 CH_2 each, pyrrolidine); 50.0, 42.0, 34.4, 29.6, and 29.4 (CH_2 each, C9, C10, C3′−C5′). MS (70 eV), *m/e* (%): 367 (45) [M$^+$], 296 (100) [M$^+$ − HNC_4H_8], 267 (80), 252 (80). Anal. Calcd for $C_{27}H_{29}N$ (367.5): C, 88.24; H, 7.95; N, 3.81. Found: C, 88.36; H, 8.19; N, 3.86.

4-Phenyl-2-pyrrolidino-7-methoxy-1,2,9,10-tetrahydro-1,2-cyclopentanophenanthrene (8b). Pentacarbonyl(7-methoxy-4-phenyl-9,10-dihydro-2*H*-benzo[*d*]chromen-2-ylidene)chromium (**5b**) (240 mg, 0.50 mmol) in 1 mL of C_6D_6, with hexamethylbenzene as an internal standard, is reacted with 1-pyrrolidinocyclopentene (**6**) (68.5 mg, 0.50 mmol) as described above for 20 h at 20 °C. According to the ^{1}H NMR spectrum, compound **8b** has been formed as the only detectable product. Chromatography gives colorless **8b** (369 mg, 93 %, R_f = 0.5 in acetone/water 10:1, detected on silica gel after exposure to iodine vapors, colorless crystals from dichloromethane/pentane 1:20 at −15 °C, mp 147−148 °C). Reaction of pentacarbonyl (7-methoxy-4-phenyl-9,10-dihydro-2*H*-benzo[*d*]chromen-2-ylidene)tungsten (**5d**) with **6** for 12 h at 20 °C affords **8b** as the only detectable organic product. ^{1}H NMR (C_6D_6): δ 7.32 and 7.07 (2:3 H, Ph); 6.78, 6.68, and 6.29 (1 H each, d, d, dd; ^4J = 1.5 Hz, ^3J = 8.5, ^3J = 8.5, and ^4J = 1.5; 5-H, 6-H, and 8-H), 5.66 (1 H, s, 3-H), 3.24 (3 H, s, OMe); 2.78, 2.50, 2.20, and

2.12 (1 H each, m each, 9-H_2 and 10-H_2), 2.61 and 1.56 (4 H each, m each, pyrrolidine), 2.36 (1 H, dd, ^3J = 8.5 and 8.5 Hz, 1-H); 2.18 and 2.05 (1 H each, m each, 5′-H_2); 1.90, 1.65, and 1.54 (1:1:2 H, m each, 4′-H_2 and 3′-H_2). ^{13}C NMR (C_6D_6): δ 157.9 (Cq, C-7); 143.1, 142.2, 140.1, 138.4, 127.1, and 125.3 (Cq each, C4, C4a, C4b, 8a, 10a, and *i*-C Ph); 128.8, 128.7, and 128.4 (1:2:2, CH each, Ph); 128.5, 127.2, 114.4, and 110.8 (1:1:1:1, CH each; C5, C6, C8, and C3), 63.3 (Cq, C2), 54.6 (CH, C1), 47.3 and 23.9 (2 CH_2 each, pyrrolidine); 50.0, 40.1, 34.4, 30.0, and 29.3 (CH_2 each, C9, C10, C3′−C5′). MS (70 eV), *m/e* (%): 397 (45) [M^+], 354 (30), 326 (100) [$M^+ - HNC_4H_8$]. Anal. Calcd for $C_{28}H_{31}NO$ (397.6): C, 84.59; H, 7.86; N, 3.52. Found: C, 84.66; H, 7.84; N, 3.42.

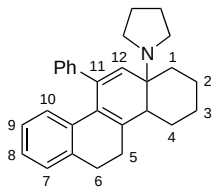
4-Acetyl-5-methyl-3-phenyl-1-pyrrolidinobicyclo[4.4.0]deca-2,4-diene (10a). Pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-



ylidene)tungsten (**3b**) (268 mg, 0.50 mmol) in 1 mL of C_6D_6 and hexamethylbenzene as an internal standard is reacted with 1-pyrrolidinocyclohexene (**9**) (75.5 mg, 0.50 mmol) for 1 h at 20 °C as described above to give colorless **10a** (291 mg, 87 %, R_f = 0.5 in acetone/water 10:1, detected on silica gel after exposure to iodine vapors, colorless crystals). ^{1}H NMR (C_6D_6): δ 7.28, 7.05, and 7.03 (2:1:2 H, Ph), 5.42 (1 H, s, 2-H), 2.59 and 1.55 (4 H each, m each, pyrrolidine), 1.99 (1 H, dd, ^3J = 6.5 and 6.5 Hz, 6-H); 1.90 and 1.86 (1 H each, m each, 7-H_2), 1.94 (3 H, s, $COCH_3$); 1.55−1.35 and 1.20−0.90 (4:2, m each, 8-H_2, 9-H_2, and 10-H_2), 1.67 (5-CH_3). ^{13}C NMR (C_6D_6): δ 202.9 (*C*OMe); 144.7, 141.7, 138.7, and 134.4 (Cq each, C3, C4, C5, and *i*-C Ph); 128.8, 127.6, 127.2, and 127.1 (2:1:2:1, CH each, C-2 and Ph), 56.1 (Cq, C1), 48.5 (CH, C6), 46.0 and 24.5 (2 CH_2 each, pyrrolidine); 41.8, 33.8, 28.8, and 25.8 (CH_2 each, C7−C10), 31.2 ($COCH_3$), 19.4 (5-CH_3). IR (diffuse reflection), cm^{-1}: 1689.2 [ν(C=O)]. MS (70 eV), *m/e* (%): 336 (5) [M^+], 320 (5), 293 (40) [M^+ − COMe], 265 (100) [$M^+ - HNC_4H_8$]. Anal. Calcd for $C_{23}H_{29}NO$ (335.5): C, 82.34; H, 8.71; N, 4.18. Found: C, 82.43; H, 8.87; N, 4.32.

4-Carboethoxy-5-methyl-3-phenyl-1-pyrrolidinobicyclo[4.4.0]-deca-2,4-diene (10b). Pentacarbonyl(5-carbethoxy-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (**3c**)[21] (276 mg, 0.50 mmol) in 1 mL of C_6D_6, with hexamethylbenzene as an internal standard, is reacted with 1-pyrrolidinocyclohexene (**9**) (75.5 mg, 0.50 mmol) as described above to give colorless **10b** (333 mg, 95 %, R_f = 0.5 in acetone/water 10:1, detected on silica gel after exposure to iodine vapor, colorless crystals). ^{1}H NMR (C_6D_6): δ 7.38 and 7.18−7.05 (2:3 H, Ph), 5.45 (1 H, s, 2-H), 3.12 (3 H, s, OCH_3), 2.72 and 2.62 (2 H each, m each, NCH_2 each, pyrrolidine), 2.08 (3 H, s, 5-CH_3), 1.99 (1 H, dd, ^3J = 3.8 and 4.3 Hz, 6-H); 1.86 and 1.76 (1 H each, m each, 7-H_2), 1.58 (4 H, m, NCH_2-C*H*$_2$-C*H*$_2$, pyrrolidine); 1.50, 1.40, and 1.16−1.12 (2:1:3 H, m each, 8-H_2, 9-H_2, and 10-H_2). ^{13}C NMR (C_6D_6): δ 169.0 (CO_2Me); 148.4, 142.3, 139.5, and 125.7 (Cq each, C3, C4, C5, and *i*-C Ph); 128.4, 127.1, 126.8, and 126.5 (2:1:2:1, CH each, C-2 and Ph), 56.6 (Cq, C1), 50.7 (OCH_3), 48.0 (CH, C6), 46.2 and 24.0 (2 CH_2 each, pyrrolidine); 34.9, 28.9, 24.5, and 23.2 (CH_2 each, C7−C10), 19.4 (5-CH_3). IR (diffuse reflection), cm^{-1}: 1717.4 [ν(C=O)]. MS (70 eV), *m/e* (%): 352 (10) [$M^+ + 1$], 351 (35) [M^+], 336 (15) [$M^+ - CH_3$], 308 (15), 294 (25), 292 (25) [$M^+ - CO_2$Me], 280 (50), 249 (70), 86 (72), 86 (100); HRMS (Ref = 342.97927) for $C_{23}H_{29}NO_2$: m/e 351.21899 (calcd. 351.21983).

11-Phenyl-12a-pyrrolidino-1,2,3,4,4a,12a,5,6-octahydrochrysene (11) and 11-Phenyl-1,2,3,4,5,6-hexahydrochrysene (12). Pentacarbonyl(4-phenyl-9,10-dihydro-2*H*-benzo[*d*]chromen-2-ylidene)chromium (**5a**) (225 mg, 0.50 mmol) in 1 mL of C_6D_6, with hexamethylbenzene as an internal standard, is reacted with 1-pyrrolidinocyclohexene (**9**) (75.5 mg, 0.50 mmol) as described above for 25 h at 20 °C. According to the ^{1}H NMR spectrum, compound **11** has been



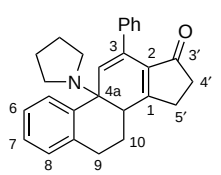
formed as the only detectable product. Chromatography gives colorless **11** (343 mg, 90%, R_f = 0.5 in acetone/water 10:1, detected on silica gel after exposure to iodine vapor, colorless crystals from dichloromethane/pentane 1:5 at −15 °C). Heating of **11** in C_6D_6 at 70 °C for ca. 3 days failed to form **12** by elimination of pyrrolidine; however, this readily occurred upon chromatographic isolation of **11** and subsequent standing at 20 °C for ca. 1 day in C_6D_6.

11. ^{1}H NMR (C_6D_6): δ 7.25 and 7.06 (2:3 H, Ph); 7.02, 6.86, and 6.73 (1:1:2 H, d, m, m, 7-H−10-H), 5.72 (1 H, s, 12-H); 2.72, 2.59, 2.25, and 1.98 (1 H each, m each, 5-H_2 and 6-H_2), 2.60 and 1.44 (4 H each, m each, pyrrolidine), 2.15 (1 H, dd, ^3J = 12.5 and 4.0 Hz, 4a-H); 2.18 and 1.85 (1 H each, m each, 4-H_2), 1.64 (2 H, m each, 3-H_2), 1.22−1.00 (4H, m, 2-H_2 and 1-H_2). ^{13}C NMR (C_6D_6): δ 145.7, 142.5, 140.2, 136.6, 134.1, and 127.1 (Cq each, C5a, C6a, C10a, 10b, 11, and *i*-C Ph); 130.3 (CH, C12); 128.9, 128.1, and 127.6 (2:2:1, CH each, Ph); 127.3, 127.2, 126.2, and 125.9 (1:1:1:1, CH each, C7−C10), 56.4 (Cq, C12a), 46.4 and 24.0 (2 CH_2 each, pyrrolidine), 46.0 (CH, C4a); 47.4, 35.0, 28.3, 25.0, and 23.2 (CH_2 each, C5, C6, C1−C4). MS (70 eV), *m/e* (%): 367 (45) [M^+], 296 (100) [$M^+ - HNC_4H_8$], 267 (80), 252 (80). Anal. Calcd for $C_{28}H_{31}N$ (381.6): C, 88.14; H, 8.19; N, 3.67. Found: C, 88.32; H, 8.35; N 3.75.

12. ^{1}H NMR (C_6D_6): δ 7.33, 6.93 and 6.77 (2:1:1 H, m, q, q, 7-H−10-H), 7.12 (5 H, Ph), 7.02 (1 H, s, 12-H), 2.67 (4 H, m, 5-H_2 and 6-H_2), 2.59 and 2.46 (1:3 H, m each, 1-H_2 and 4-H_2), 1.62 (4 H, m, 2-H_2 and 3-H_2). ^{13}C NMR (C_6D_6): δ 144.4, 139.0, 135.2, 128.6, 128.4, 128.1, 127.9, and 127.8 (Cq each, C4a, C5a, C6a, C10a, C10b, C11, C12a, and *i*-C Ph); 131.2 (CH, C12); 130.1, 128.7, and 128.3 (2:2:1, CH each, Ph); 129.9, 127.3, 126.6, and 125.7 (1:1:1:1, CH each, C7−C10); 30.4, 29.9, 27.1, 25.8, 23.9, and 23.1 (CH_2 each, C5, C6, C1−C4). MS (70 eV), *m/e* (%): 312 (40) [$M^+ + 2$], 310 (75) [M^+], 296 (15), 282 (25), 270 (60), 253 (65), 241 (80), 239 (45), 119 (100); HRMS (Ref = 304.98246) for $C_{24}H_{22}$: *m/e* 310.17142 (calcd.310.17215).

5-Phenyl-8,9,10,11,12,13-hexahydro-7*H*-cyclohepta[*a*]phenanthrene (15). Pentacarbonyl(4-phenyl-9,10-dihydro-2*H*-benzo[*d*]chromen-2-ylidene)chromium (**5a**) (225 mg, 0.50 mmol) in 1 mL of C_6D_6, with hexamethylbenzene as an internal standard, is reacted with 1-morpholinocycloheptene (**13**) (93.5 mg, 0.50 mmol) as described above for 18 h at 90 °C. Chromatography gives colorless **15** (57 mg, 35 %, R_f = 0.5 in pentane, detected on silica gel after exposure to iodine vapors, colorless crystals from pentane at −15 °C, mp 145 °C). ^{1}H NMR (C_6D_6): δ 7.30, 7.18, 6.85, and 6.70 (2:6:1:1 H, m each); 2.80, 1.81, and 1.53 (8:2:4 H, m each). ^{13}C NMR (C_6D_6): δ 144.3, 143.0, 139.8, 139.0, 138.0, 137.9, 135.4, and 131.9 (Cq each); 131.0 and 130.7 (2 C), 130.2 and 128.7 (2 C), 127.2, 126.6, 126.4, and 125.8 (CH each); 36.6, 32.6, 30.3, 29.8, 28.7, 27.6, and 27.1 (CH_2 each). MS (70 eV), *m/e* (%): 324 (100) [M^+], 281 (10), 267 (30), 254 (20). Anal. Calcd for $C_{24}H_{24}$ (324.5): C, 92.54; H, 7.46. Found: C, 92.43; H, 7.81.

3-Phenyl-4a-pyrrolidino-4a,9,10,10a-tetrahydro-1,2-(3-oxocyclopenteno)phenanthrene (18) and 3-Phenyl-9,10-dihydro-1,2-(3-oxocyclopenteno)phenanthrene (19). To pentacarbonyl(9-oxo-4-phenyl-



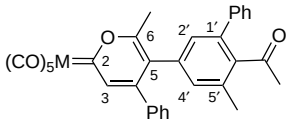
5,6-cyclopenteno-2*H*-pyran-2-ylidene)chromium (**17a**) (201 mg, 0.50 mmol) in 1 mL of C_6D_6, with hexamethylbenzene as an internal standard, is reacted with 1-pyrrolidino-3,4-dihydronaphthalene (**16**) (100 mg, 0.50 mmol) as described above. According to the ^{1}H NMR spectrum compound **18** has been formed as the only detectable product. Chromatography on silica gel affords colorless **19**.

(21) Roths, K. Dissertation, Münster, 1996.

18. ^{1}H NMR (600 MHz, C_6D_6): δ 8.09 (1 H, d, ^3J = 8.0 Hz, 5-H), 7.43, 7.24, and 7.20 (2:2:1 H, Ph), 7.12 and 7.10 (1 H each, t each, 6-H and 7-H), 7.06 (1 H, d, ^3J = 7.7 Hz, 8-H), 5.42 (1 H, s, 4-H), 3.61 (1 H, m, 10a-H), 3.15 and 2.57 (2 H each, 2 NCH_2 pyrrolidine); 2.92, 2.79, 2.62, and 2.58 (1 H each, m each, 9-H_2 and 10-H_2), 1.96 (2 H, m, 4′-H_2), 1.63 and 1.60 (2 H each, 2 N-CH_2-CH_2, pyrrolidine), 1.32 (2 H, m, 5′-H_2). ^{13}C NMR (C_6D_6): δ 208.5 (Cq, C═O), 167.4 (Cq, C1), 140.5, 138.8, 137.5, 134.4, and 133.9 (Cq each, C2, C3, C4b, 8a, and *i*-C Ph); 128.4, 128.3, and 127.9 (2:2:1, CH each, Ph); 127.6, 127.4, 126.7, and 125.6 (1:1:1:1, CH each, C5−C8), 100.8 (CH, C4), 74.3 (CH, C10a), 70.0 (Cq, broad, C4a), 47.2 (2 NCH_2), 41.8 and 26.9 (CH_2 each, C9 and C10), 29.9 (CH_2, C4′), 24.7 (NCH_2-CH_2-CH_2), 23.4 (CH_2, C5′). MS (70 eV), *m/e* (%): 381 (15) [M^+], 310 (100) [$M^+ - C_4H_8$-NH], 309 (80), 281 (40), 265 (60), 252 (60). Anal. Calcd for $C_{27}H_{27}$-NO (381.5): C, 85.00; H, 7.13; N, 3.67. Found: C, 85.10; H, 7.24; N, 3.82.

19. ^{1}H NMR (C_6D_6): δ 7.84, 7.35 and 7.25 (2:2:1 H, Ph), 7.64 (1 H, s, 4-H), 7.50 and 7.10 (1:3 H, m each, H-5−H-8), 2.60 and 2.40 (2 H each, m each, 4′-H_2 and 5′-H_2), 2.23 (4 H, s, 9-H_2 and 10-H_2). ^{13}C NMR (C_6D_6): δ 203.6 (Cq, C═O), 154.1 (Cq, C1), 140.2, 139.2, 139.1, 137.9, 134.0, 133.2, and 132.7 (Cq each, C2, C3, C4a, C4b, 8a, 10a, and *i*-C Ph); 130.4, 129.1, and 128.4 (2:1:2, CH each, Ph); 128.8, 128.2, 127.9, 126.1, and 125.9 (1:1:1:1:1, CH each, C5′−C8 and C4), 36.9, 28.6, 23.8, and 23.6 (CH_2 each, C9, C10, C4′ and C5′). MS (70 eV), *m/e* (%): 311 (60) [M^+ = 1], 310 (100) [M^+], 309 (80) [$M^+ - 1$], 281 (40), 265 (60), 252 (60). Anal. Calcd for $C_{23}H_{18}O$ (310.4): C, 89.00; H, 5.85. Found: C, 89.35; H, 5.96.

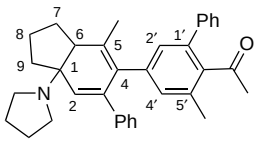
Pentacarbonyl[5-(6′-acetyl-5′-methylbiphenyl-3′-yl)-6-methyl-4-phenyl-2*H*-pyran-2-ylidene]chromium (20a). To pentacarbonyl(5-



acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)chromium (**3a**) (404 mg, 1.00 mmol) in acetone (3 mL) in a 5-mL screwtop vessel is added triethylamine (50 mg, 0.50 mmol). A TLC after 15 h at 20 °C indicates complete consumption of starting material, while $Cr(CO_6)$ and a cherry-red compound **20a** are produced. Chromatography on silica gel affords **20a** (242 mg, 85 %, R_f = 0.5 dichloromethane/pentane 1:1, red crystals from diethyl ether/pentane). ^{1}H NMR ($CDCl_3$): δ 8.06 (1 H, s, 3-H), 7.30 (6 H, m, *o*- and *m*-H each, 2 Ph), 7.10 and 7.03 (2 H each, m each, *o*-H each, 2 Ph), 6.89 and 6.74 (1 H each, s, 2′-H and 4′-H), 2.61 (3 H, s, 6-CH_3), 2.21 (3 H, s, 6′-CH_3), 1.82 (3 H, s, $OCCH_3$). ^{13}C NMR ($CDCl_3$): δ 279.5 (Cr═C), 224.0 and 217.8 [*trans*- and *cis*-CO, $Cr(CO)_5$], 206.8 (Cq, O*C*CH_3), 175.7 (Cq, C6), 143.8 (Cq, C4), 141.1 (Cq, C1′), 139.3 (CH, C3); 139.2, 139.1, and 133.8 (Cq each, C3′, C5′, and C6′); 135.5 and 134.6 (Cq each, *i*-C each, 2 Ph); 130.9, 129.6, 129.2, 129.1, 128.6, 128.5, 128.4, and 128.1 (1:1:1:2:2:2:2:1, CH each, 2 Ph and C2′, C4′), 125.3 (Cq, C5), 31.8 (6-CH_3), 20.2 (6′-CH_3), 19.5 (O*C*CH_3). IR (diffuse reflection), cm^{-1}: 2052.5, 1977.1, 1917.2 [ν-(C≡O)], 1697.1 [ν(C═O)]; IR (hexane): 2053.5 (30), 1977.8 (5), 1937.8 (100) [ν(C≡O)]. MS (70 eV), *m/e* (%): 570 (20) [M^+], 514 (10), 486 (20), 458 (60), 430 (100) [$M^+ - 5CO$]. Anal. Calcd for $C_{32}H_{22}CrO_7$ (570.5): C, 67.37; H, 3.89. Found: C, 67.51; H, 3.96.

Pentacarbonyl[5-(6′-acetyl-5′-methylbiphenyl-3′-yl)-6-methyl-4-phenyl-2*H*-pyran-2-ylidene]tungsten (20b). To pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (**3b**) (536 mg, 1.00 mmol) in acetone (3 mL) in a 5-mL screwtop vessel is added triethylamine (50 mg, 0.50 mmol). A TLC after 15 h at 20 °C indicates complete consumption of starting material, while $W(CO_6)$ and a cherry-red compound **20b** are formed. Chromatography on silica gel affords **20b** (288 mg, 82 %, R_f = 0.5 dichloromethane/pentane 1:1, red crystals from diethyl ether/pentane). ^{1}H NMR ($CDCl_3$): δ 8.09 (1 H, s, 3-H), 7.35 (6 H, m, *o*- and *m*-H each, 2 Ph), 7.12 and 7.08 (2 H each, m each, *o*-H each, 2 Ph), 6.97 and 6.81 (1 H each, AX-system, ^4J = 1.7 Hz, 2′-H and 4′-H), 2.61 (3 H, s, 6-CH_3), 2.26 (3 H, s, 6′-CH_3), 1.89 (3 H, s, $OCCH_3$). ^{13}C NMR ($CDCl_3$): δ 255.4 (W═C), 206.7 (Cq, O*C*CH_3), 204.4 and 198.7 [*trans*- and *cis*-CO, $W(CO)_5$], 174.6 (Cq, C6), 147.0 (Cq, C4), 141.6 (CH, C3), 141.2 (Cq, C1′); 139.2, 139.1, and 133.8 (Cq each, C3′, C5′, and C6′); 135.6 and 134.6 (Cq each, *i*-C each, 2 Ph); 131.3, 130.9, 129.7, 129.3, 129.1, 129.0, 128.9, and 128.5 (1:1:1:2:2:2:2:1, CH each, 2 Ph and C2′, C4′), 126.1 (Cq, C5), 31.8 (6-CH_3), 20.8 (6′-CH_3), 19.5 (O*C*CH_3). IR (diffuse reflection), cm^{-1}: 2059.5, 1975.3, 1912.3 [ν(C≡O)], 1697.4 [ν(C═O)]. MS (70 eV), ^{184}W, *m/e* (%): 702 (20) [M^+], 674 (10), 618 (50), 590 (30), 562 (80) [$M^+ - 5CO$], 352 (100) [$W(CO)_6$]. Anal. Calcd for $C_{32}H_{22}O_7W$ (702.4): C, 54.72; H, 3.16. Found: C, 54.51; H, 3.06.

4-(6′-Acetyl-5′-methylbiphenyl-3′-yl)-5-methyl-3-phenyl-1-pyrrolidinobicyclo[4.3.0]nona-2,4-diene (21). To pentacarbonyl[5-(6′-



acetyl-5′-methylbiphenyl-3′-yl)-6-methyl-4-phenyl-2*H*-pyran-2-ylidene]-tungsten (**20b**) (336 mg, 1.00 mmol) in 1 mL of C_6D_6, with hexamethylbenzene as an internal standard, is reacted with 1-pyrrolidinocyclopentene (**6**) (68.5 mg, 0.50 mmol) as described above. According to the ^{1}H NMR spectrum, compound **21** has been formed as the only detectable product. Chromatography gives colorless **21** (438 mg, 90 %, R_f = 0.5 in acetone/water 10:1, detected on silica gel after exposure to iodine vapors, colorless crystals from dichloromethane/pentane 1:20 at −15 °C). ^{1}H NMR (C_6D_6): δ 7.20−6.90 (12 H, 2 Ph and 2′-H, 4′-H), 5.56 (1H, s, 3-H), 2.70 and 1.60 (4 H each, m each, pyrrolidine), 2.40 (1 H, dd, ^3J = 9 and 9 Hz, 8-H); 2.23 and 1.90 (1:1 H, m each, 7-H_2); 2.20, 1.80, and 1.65 (3 H each, s each, CH_3 each); 1.80, 1.40, and 1.25 (1:1:2, m each, 8-H_2 and 9-H_2). ^{13}C NMR (C_6D_6): δ 203.9 (Cq, *O*CCH_3); 142.8, 141.8, 141.2, 141.1, 139.7, 138.6, 138.3, 133.2, and 131.9 (Cq each, C3, C4, C5, C1′, C3′, C5′, C6′, and 2 *i*-C Ph); 130.0, 129.2, 129.1, 129.0, 128.6, 126.4, and 125.8 (1:2:2:1:2: 2:1:1, CH each, 2 Ph and C2′, C4′), 63.4 (Cq, C1), 51.6 (CH, C8), 46.9 and 24.1 (2 CH_2 each, pyrrolidine); 51.2, 41.9, and 35.3 (CH_2 each, C7−C9); 23.7, 20.9, 19.6 (CH_3 each). MS (70 eV), *m/e* (%): 487 (45) [M^+], 416 (100) [$M^+ - HNC_4H_8$], 402 (60). Anal. Calcd for $C_{35}H_{37}NO$ (487.7): C, 86.20; H, 7.65; N, 2.87. Found: C, 86.43; H, 7.79; N, 3.02.

Pentacarbonyl[5-acetyl-4-phenyl-6-(2-phenylethenyl)2*H*-ylidene]-tungsten (22b). Pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (**3b**) (268 mg, 0.50 mmol), triethylamine (303 mg, 3.00 mmol), chlorotrimethylsilane (163 mg, 1.50 mmol), and benzaldehyde (53 mg, 0.50 mmol) in 3 mL of dry diethyl ether in a 5-mL screwtop vessel, is stirred 3 d at 55 °C to give a dark-blue solution. Chromatography on silica gel with pentane/dichloromethane (3:1) affords **22b** (60 mg, 19 %, R_f = 0.4 in pentane/dichloromethane (3:1), mp 143 °C). ^{1}H NMR (C_6D_6): δ 8.20 and 6.90 (1 H each, d each, AB-system, ^3J = 16 Hz, CH═CHPh), 7.88 (1 H, s, 3-H), 7.33 and 7.05−6.95 (2:8 H, m each, 2 Ph), 1.23 (3 H, s, $COCH_3$). ^{13}C NMR (C_6D_6): δ 256.2 (W═C), 204.1 and 199.3 [*trans*- and *cis*-CO, $W(CO)_5$], 199.2 (Cq, C═O), 168.1 (Cq, C6), 143.3 (Cq, C4), 142.1 (CH═*C*HPh), 141.0 (CH, C3), 135.7 and 135.1 (Cq each, *i*-C each, 2 Ph); 131.3, 131.2, 129.9, 129.7, 129.1, and 128.4 (1:1:2:2:2:2, CH each, 2 Ph), 127.1 (Cq, C5), 116.5 (*C*H═CHPh), 31.3 (CO*C*H_3). IR (diffuse reflection), cm^{-1}: 2057.9, 1973.9, 1918.0 [ν(C≡O)], 1699.0 [ν(C═O)]; IR (hexane): 2060.0 (30), 1973.1 (5), 1936.4 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m/e* (%): 624 (60) [M^+], 596 (20), 540 (60), 545 (50) [$M^+ - 5CO$], 268 (100). Anal. Calcd for $C_{26}H_{16}O_7W$ (624.3): C, 50.03; H, 2.58. Found: C, 50.22; H, 2.62.

Acknowledgment. This investigation was supported by the Volkswagen-Stiftung and the Fonds der Chemischen Industrie. We thank Beate Jasper for experimental assistance.

Supporting Information Available: Tables of positional and displacement parameters, bond distances, and angles (8 pages). See any current masthead page for ordering and Internet access instructions.

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