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Organic Syntheses *via* Transition Metal Complexes. 85.[1] [2-(Alkenyloxy)ethenyl]- and [2-(Aryloxy)ethenyl]carbene Complexes from (1-Alkynyl)carbene Complexes of Chromium and Tungsten and Their Fragmentation to 2,4-Dien-5-ones

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[2-(Alkenyloxy)ethenyl]carbene complexes $(CO)_5M{=}C(OEt)CH{=}C(O\text{-alkenyl})Ph$ (**3**) (M = Cr, W) are obtained by base-catalyzed *O*-addition of enolizable 1,3-diones **2** (cyclopentane-1,3-dione and dimedone) to (1-alkynyl)carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CPh$ (**1**) (M = Cr, W) together with pyran-2-ylidene complexes **4**, which are generated by *C*-addition of the enolate unit of **2**. Thermal fragmentation of the *O*-addition products **3** affords dienones **5**, resulting from overall C_3 insertion of the (1-alkynyl)carbene ligand of **1** into a C,O bond of **2**. Both, *O*- and *C*-addition products, **7** and **8**, respectively, are derived from reaction of 9-phenanthrol (**6**) with **1** in a ratio 2:1, but phenol (**9a**) and 2-naphthol (**9b**) yield [2-(aryloxy)-ethenyl]carbene complexes $(CO)_5M{=}C(OEt)CH{=}C(OAr)Ph$ (**10**) (M = Cr, W; Ar = Ph, 2-naphthyl) only (81−91%). Addition of **9** is highly regio- and stereoselective and affords stereoisomers (*E*)-**10** initially, which undergo (*E*/*Z*) isomerization in solution to give isomers (*Z*)-**10**. Binuclear carbene complexes **12**, **14**, and **16** [$(CO)_5M{=}C(OEt)CH{=}C(Ph)OArO(Ph)C{=}CH(OEt)C{=}M(CO)_5$ (M = Cr, W)] are obtained from dihydroxyaryl compounds $Ar(OH)_2$ (Ar = 1,4-phenylene, 1,3-phenylene, 1,1′-binaphthyl). Addition of cyclohexyl isocyanide (**17**) to (*Z*)-**10** results in formation of a ketenmine complex $(CO)_5Cr[CyN{=}C{=}C(OEt)CH{=}C(OPh)Ph]$, which in the presence of water and (excess) **17** affords an (1-amino)-ketocarbene complex $(CO)_5Cr{=}C(NHCy)C({=}O)CH{=}C(OPh)Ph$ (**18**) and an amide $(CyNH)C({=}O)CH(OEt)CH{=}C(OPh)Ph$ (**19**). X-ray data are reported for compounds (*Z*)-**3b**, (*E*)-**10d**, and (*E*,*E*)-**12a**.

1-Metalla-2,4-dioxy-1,3-butadienes. 1-Metalla-1,3-butadienes[2] (=alkenylcarbene complexes) of chromium and tungsten have gained much interest as C_3 building blocks for the synthesis of carbocyclic and heterocyclic ring compounds.[3,4] Among the broad array of 1-metalla-1,3-dienes the 2,4-dioxy derivatives $(CO)_5M{=}C(OEt)CH{=}CR(OR^1)$ (M = Cr, W) deserve special attention with regard to the structural relationship to 1,3-dicarbonyl equivalents and the synthethic implications based on such a relationship. 1-Metalla-1,3-butadienes have been prepared as early as 1967,[5] but systematic studies were initiated only recently. Several methods are available for the generation of complexes $(CO)_5M{=}C(OEt)C{=}CR(O\text{-alkyl})$ (M = Cr, W) containing an *enol ether* unit. They include (a) condensation of methylcarbene complexes $(CO)_5M{=}C(OEt)CH_3$ with nonenolizable acid amides $R^1{-}CONR_2$,[6] (b) reaction of enolizable acid amides $R^1CH_2{-}CONR_2$ with carbene complexes $(CO)_5M{=}C(OEt)R$ involving insertion of the CCN backbone into the M=C bond,[7] (c) insertion of an alkyne group into the M=C bond of an alkoxycarbene complex,[6b,8,9] and (d) addition of alcohols to an (1-alkynyl)carbene complex.[10−12] The latter method has been utilized, e.g.,

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(1) Part 84 of this series: Aumann, R.; Jasper, B.; Fröhlich, R. *Organometallics* **1996**, *15*, 1942.

(2) The term 1-metalla-1,3-butadiene and also 1-metalla-1,3,5-hexatriene has been suggested (see: Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537−540) to allow for a simple systematic nomenclature of alkenylcarbene complexes with different substitution pattern and different stereochemistry.

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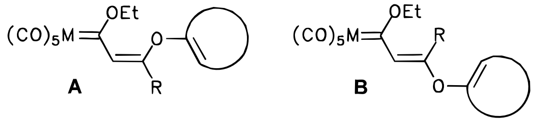
Scheme 1. 2-(Alken-1-yloxy)ethenyl]carbene Complexes (M = Cr, W)



to introduce carbohydrates as chiral inductors[12] into a 1-metalla-1,3-butadiene. Complexes $(CO)_5M{=}C(OEt)C{=}CR(O\text{-acyl})$ (M = Cr, W), which contain an *enol ester* unit, are quite different in reactivity from corresponding enol ethers. Such compounds are available (e) by condensation of methylcarbene complexes with acid chlorides[13,14] and (f) by addition of carboxylic acids to (1-alkynyl)carbene complexes.[15]

While pursuing studies on 1-metalla-2,4-dioxy-1,3-butadienes, we found an access to the new class of *divinyl ether* derivatives (*E*/*Z*)-$(CO)_5M{=}C(OEt)CH{=}CR(O\text{-alkenyl})$ [M = Cr, W (**A**, **B**)] (Scheme 1) by Michael-type addition of enolizable carbonyl compounds to an (1-alkynyl)carbene complex **1a**,**b**.

***O*-Alkenylation of Carbonyl Compounds.** Though it is well documented that alcohols or phenols yield Michael-type adducts with an (1-alkynyl)carbene complex, e.g. **1a**,**b**,[12,16,17,24] formation of divinyl ether compounds, e.g. **3a**,**b**, by *O*-addition of an enolizable carbonyl compound to a (1-alkynyl)carbene complex has not been reported before (Scheme 2). Addition of enolizable 1,3-dicarbonyl compounds[18,19] or α-aryl ketones[1] to **1** was reported to produce pyranylidene complexes resulting from ring closure of 1-metalla-1,3,5-trienes, which are formed as primary *C*-alkenylation products of the enolate unit.[1,19] We now wish to report that *O*-alkenylation of cyclic 1,3-dicarbonyl compounds may become the major reaction path under certain conditions. For example, addition of catalytic amounts of Et_3N to a 1:1 mixture of cyclopentane-1,3-dione (**2a**) and (1-alkynyl)carbene complex **1a**,**b** in diethyl ether results in formation of a (red) divinyl ether derivative **3a**,**b** and a (blue) pyranylidene complex **4a**,**b** in a 3:2 ratio (Scheme 2). The product ratio of **3**:**4** is influenced by solvent polarity, such that e.g. in diethyl ether more *O*-alkylation product **3** is obtained than in dichloromethane. Since both compounds, **3** and **4**, are unstable in the presence of base, much attention has to be paid to the reaction time and the concentration of the catalyst in order to achieve good chemical yields.

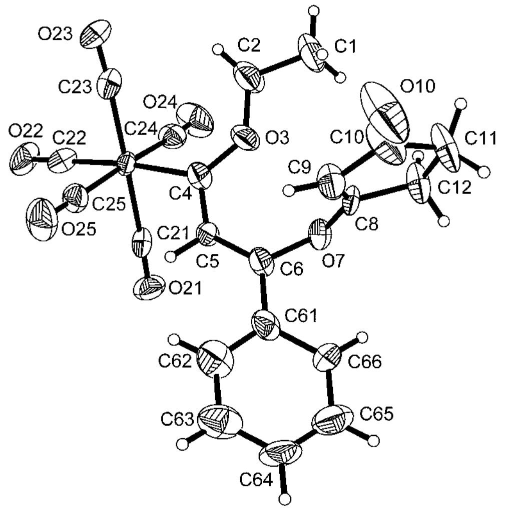
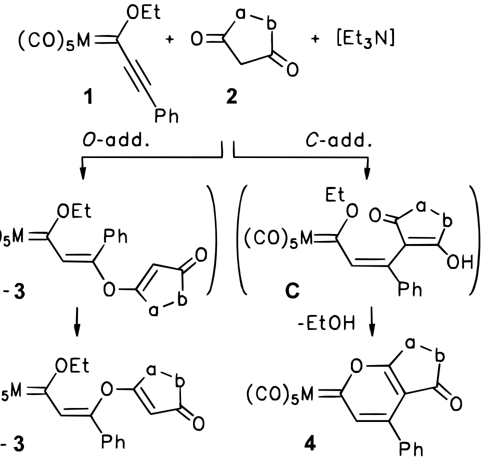


Figure 1. Molecular structure of the divinyl ether carbene complex (*Z*)-**3b**.

Scheme 2. *C*- *vs* *O*-Alkenylation of 1,3-Diones with (1-Alkynyl)carbene Complexes (M = Cr, W)



1	M	2 a-b	3,4	M	a-b	[3:4]%
a	W	a CH_2CH_2	a	W	CH_2CH_2	56:38
b	Cr	b $CH_2CMe_2CH_2$	b	Cr	CH_2CH_2	54:35
			c	W	$CH_2CMe_2CH_2$	38:52

Since reaction of phenols **9** with compounds **1** (*v.i.*) was shown to initially produce (*E*) isomers, which undergo a configurational change to (*Z*) products in solution, it can be reasonably assumed that addition of enolates to **1** would yield a stereoisomer (*E*)-**3** by kinetic reaction control, which subsequently affords the thermodynamically favored isomer (*Z*)-**3**. Only (*Z*) stereoisomers of divinyl ethers **3** have been isolated so far. The configuration of (*Z*)-**3** is assigned on the basis of NOE enhancements observed between the proton signals of the vinyl and the phenyl group C*H*=C*Ph*. More structural details were obtained from a X-ray analysis of (*Z*)-**3b** (Figure 1, Tables 1 and 2).

The distance between atoms Cr−C4 [2.057(11) Å], C4−C5 [1.442(15) Å], and C4−O3 [1.323(12) Å] of (*Z*)-**3b** are similar to those observed for $(CO)_5Cr{=}C(OMe)Ph$ [2.04(3), 1.47(4), and 1.33(2) Å].[20] Distance C4−O3 [1.323(12) Å] is much shorter than C6−O7 [1.409(12) Å] due to the carboxonium character of the former group. The plane defined by the carbene ligand bisects the angle between two neighboring carbonyl ligands, C21−Cr−C4−C5 [44.4(1)°]. Furthermore, the 1-chroma-

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Table 1. Details of the X-ray Crystal Structure Analysis of (*Z*)-3b

formula	$C_{21}H_{16}CrO_8$
a (Å)	9.536(1)
b (Å)	35.605(7)
c (Å)	6.144(1)
V ($Å^3$)	2086.1(6)
diffractometer	Enraf-Nonius MACH III
data coll temp (K)	223
λ (Å)	0.710 73
space group	$Pna2_1$ (No. 33)
Z	4
μ (cm^{-1})	5.93
empirical abs corr (%)	94.6−99.9
θ_{max} (deg)	26.33
no. of data collcd	2321
no. of unique data	2321
no. of data obsd ($\geq 2\sigma(I)$)	1342
no. of refined params	272
$R1$ ($\geq 2\sigma(I)$)	0.061
wR^2 ($\geq 2\sigma(I)$)	0.162
Flack param	0.12(8)
goodness of fit	1.054
program used	SCHAKAL-92

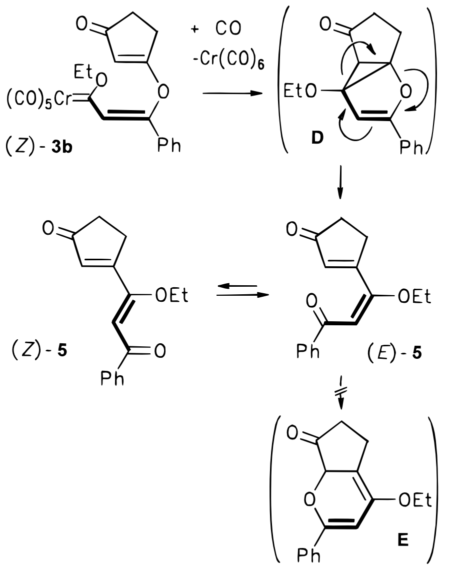
Table 2. Selected Bond Lengths (Å) and Angles (deg) for (*Z*)-3b

Cr−C(4)	2.057(11)	O(7)−C(8)	1.373(11)
C(1)−C(2)	1.489(18)	C(8)−C(9)	1.295(16)
C(2)−O(3)	1.447(14)	C(8)−C(12)	1.489(14)
O(3)−C(4)	1.323(12)	C(9)−C(10)	1.452(17)
C(4)−C(5)	1.442(15)	C(10)−O(10)	1.210(17)
C(5)−C(6)	1.358(15)	C(10)−C(11)	1.529(22)
C(6)−O(7)	1.409(12)	C(11)−C(12)	1.469(18)
C(6)−C(61)	1.467(15)		
C(22)−Cr−C(4)	174.7(5)	C(5)−C(6)−C(61)	124.7(10)
C(24)−Cr−C(4)	96.0(5)	O(7)−C(6)−C(61)	114.0(9)
C(21)−Cr−C(4)	87.8(5)	C(8)−O(7)−C(6)	116.8(8)
C(23)−Cr−C(4)	94.2(5)	C(9)−C(8)−O(7)	129.9(10)
C(25)−Cr−C(4)	86.1(5)	C(9)−C(8)−C(12)	115.4(10)
O(3)−C(2)−C(1)	106.9(12)	O(7)−C(8)−C(12)	114.7(9)
C(4)−O(3)−C(2)	122.4(9)	C(8)−C(9)−C(10)	107.5(11)
O(3)−C(4)−C(5)	109.9(9)	O(10)−C(10)−C(9)	125.3(14)
O(3)−C(4)−Cr	130.2(8)	O(10)−C(10)−C(11)	126.5(12)
C(5)−C(4)−Cr	119.9(7)	C(9)−C(10)−C(11)	108.1(11)
C(6)−C(5)−C(4)	129.0(10)	C(12)−C(11)−C(10)	104.6(9)
C(5)−C(6)−O(7)	121.1(9)	C(11)−C(12)−C(8)	104.0(11)

1,3-diene unit is essentially planar (C4−C5−C6−O7 = −3.8°) and adopts a *transoid* configuration [Cr−C4−C5−C6 = 154.8(1)°], in which the cycloalkenyloxy group is almost perpendicular to the adjacent C═C bond [C6−O7−C8−C9 = −9.1(1)°, C5−C6−O7−C8 = 99.8(1)°]. Steric interactions between the cycloalkenyloxy group and the phenyl and ethoxy substituents appear to force the cycloalkenyloxy group out of the plane of the metalladiene. Thus delocalization of electron density from O7 into the adjacent C═C bond of the 1-chroma-1,3-diene unit is expected to be smaller than into the adjacent C═C bond of the cycloalkenyl unit. Bond angles and bond distances of the O3−C4−C5−C6−O7 backbone are similar to that found for {[2-(acyloxy)-ethenyl]carbene}pentacarbonyltungsten complexes.[14]

Dienones by Fragmentation. Thermolysis of the chromium complex (*Z*)-**3b** at 80 °C for 2 h does not result in a Claisen-type *O*/*C*-rearrangement but in a novel fragmentation of the divinyl ether unit to produce a 3:1 mixture of diene diones (*E*/*Z*)-**5** by elimination of $Cr(CO)_6$. Interestingly, the overall process involves insertion of the C_3 unit of the (1-alkynyl)carbene complex **1** into the C,O bond of the carbonyl component **2** (Scheme 3).

Scheme 3. Dienone Formation by Novel Fragmentation of a Divinyl Ether Carbene Complex



Transformation of compound (*Z*)-**3** into (*E*/*Z*)-**5** is assumed to proceed *via* a homofurane intermediate **D**, on the basis of related studies of homopyrroles derived from alkyne insertion into [(vinylamino)carbene]iron complexes.[21] Homofurans of type **D** may be generated as precursors to dienediones also on the interaction of furans with metal carbenoids generated by $Rh_2(OAc)_4$-catalyzed decomposition of an α-diazo ketone.[22] Other than 1,3-dien-5-one imines,[21] cyclization of the 1,3-dien-5-one unit of compound (*E*)-**5** (to afford a pyrane **E**) has not been observed (Scheme 3). The configuration of the stereoisomers (*E*/*Z*)-**5** was determined by NOE measurements, which indicate a positive enhancement of the vinyl signal 2-H on irradiation of OCH_2 in stereoisomer (*E*)-**5** but not in (*Z*)-**5**. Compound (*E*)-**5** could be isolated by fractionating crystallization and was shown by ^1H NMR spectra to afford a 3:1 mixture of (*E*/*Z*)-**5** in solution at 20 °C within several hours.

***O*-Alkenylation of 9-Phenanthrol.** Both, *O*- and *C*-addition products, **7** (58%) and **8** (28%) are obtained from reaction of 9-phenanthrol (**6**) with (1-alkynyl)-carbene complex **1b** in presence of Et_3N (Scheme 4). Compound **7** forms stereoisomers (*E*)-**7** and (*Z*)-**7**, both of which were isolated and fully characterized.

Enol Ethers 10. Other than enolizable 1,3-carbonyl compounds **2** or 9-phenanthrol (**6**), phenols do not afford *C*- but *O*-alkylation products only. (1-Alkynyl)carbene complexes **1a**,**b** add phenol (**2a**) in presence of catalytic amounts of Et_3N at 0 °C to give enol ethers **10** (Scheme 5). The reaction is initiated by formation of an allenide complex,[23] from which the stereoisomer (*E*)-**10** is obtained through kinetic control of the protonation site.[24] Compounds (*E*)-**10** can be isolated in brick-red crystals

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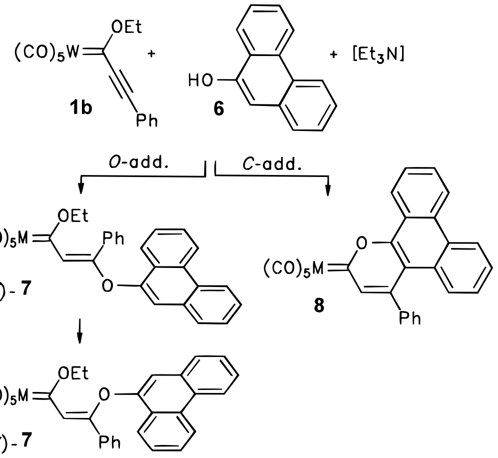
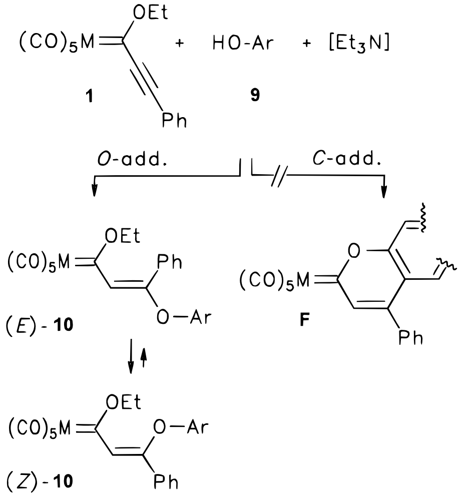
(24) The configurational assignment of the phenol derivative **10b** is different from what has been reported before in refs 16 and 17.

Scheme 4. *O*- and *C*-Alkenylation of 9-Phenanthrol



Scheme 5. 1-Metalla-2,4-dioxy-1,3-butadienes 10 by Michael Addition of Aryloxy Compounds 9 to (1-Alkynyl)carbene Complexes



1	M	**9**	Ar
a	W	**a**	Ph
b	Cr	**b**	2-Naph[c]

10	M	Ar	[**10**] %	E/Z kin[a]	E/Z therm[b]
a	W	Ph	91	10:1	1:3
b	Cr	Ph	81	10:1	2:3
c	W	2-Naph[c]	85	8:1	2:5
d	Cr	2-Naph[c]	87	6:1	2:3

[a] (*E/Z*) isomer ratio formed initially. [b] (*E/Z*) isomer ratio after equilibration at 50 °C. [c] 2-naphthyl

by fractionating crystallization. They exhibit configurational stability in the solid state but undergo facile (*E*/*Z*) isomerization at the C=C(OAr)Ph bond in solution, which is weakened by polarization of capto-dative bond system $(CO^-)_5MC(OEt)=CHC(=O^+Ar)Ph$. An attempt to isolate compounds (*E*)-**10** by chromatography inevitably results in production of mixtures of (*E*/*Z*)-**10**. Furthermore, stereoisomers (*Z*)-**10** are more stable than the corresponding compounds (*E*)-**10** and thus are accumulated in the mother liquor of the reaction mixture at 20 °C. Isomers (*Z*)-**10** can be isolated by crystallization from "enriched" reaction mixtures. They form dark red crystals, quite different in color and appearance from those of corresponding isomers (*E*)-**10**. According to NMR measurements mixtures of identical (*E*/*Z*) isomeric ratio are produced in solution at 20 °C and (more rapidly) at 50 °C from both isomers (*E*)-**10** and (*Z*)-**10**. It should be noted that compounds **10** represent one of the up to date rare examples for which both (*E*) and (*Z*) isomers of 1-metalla-1,3-dienes were isolated separately and were shown to be interconverted to identical (*E*/*Z*) mixtures.[25]

Table 3. Selected (^{13}C and ^{1}H) NMR Shifts (*δ* Values) and *ν*(C=C) IR Frequencies (cm^{-1}) of Compounds (*E*)-10 and (*Z*)-10

10	M	Ar	δ(M=C)	δ(C4)	δ(*i*-C,Ar)	δ(3-H)	ν(C=C)
(*E*)-**10a**	W	Ph	300.7	154.0	161.0	7.08	1552.8
(*Z*)-**10a**	W	Ph	303.8	148.5	157.7	7.65	1558.9
(*E*)-**10b**	Cr	Ph	328.5	154.1	157.8	7.07	1551.7
(*Z*)-**10b**	Cr	Ph	331.5	144.9	157.0	7.68	1558.5
(*E*)-**10c**	W	2-naph[a]	300.7	151.4	160.8	7.07	1548.5
(*Z*)-**10c**	W	2-naph[a]	304.1	148.3	155.2	7.76	1557.2
(*E*)-**10d**	Cr	2-naph[a]	328.6	151.7	157.2	7.07	1552.2
(*Z*)-**10d**	Cr	2-naph[a]	332.1	144.4	155.3	7.74	1559.0

[a] 2-Naphthyl.

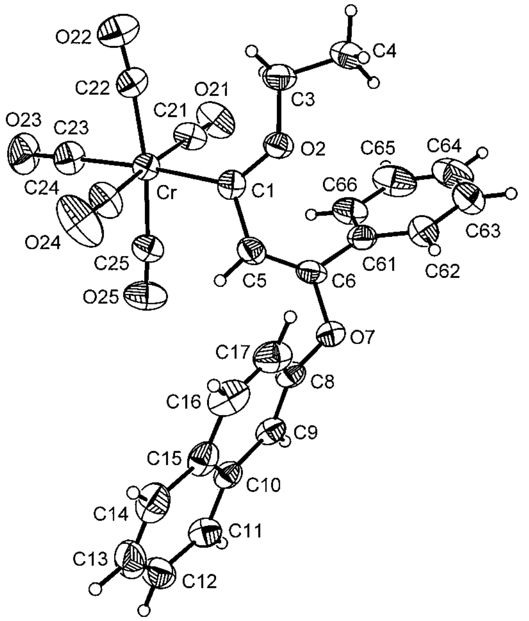


Figure 2. Molecular structure of 1-chroma-1,3-diene (*E*)-**10d**.

Apart from the different color of crystalline (*Z*)-**10** and (*E*)-**10**, as the most simple means for discrimination of such isomers, the configurational assignment of compounds **10** is based on NMR and IR data (Table 3). The carbon signals C4 and *i*-C Ar in the ^{13}C NMR spectra of (*Z*)-**10** are characteristically shifted to lower field by a *γ*-effect. A strong downfield shift of 0.6–0.7 ppm is observed also for the hydrogen signal of 3-H in compounds (*Z*)-**10**, due to the anisotropic influence of the neighboring phenyl group. In the IR spectra a slight hypsochromic shift of the *ν*(C=C) band seems to be associated with the (*Z*) configuration of **10**.

As can be seen from the X-ray structure analysis of compound (*E*)-**10d** (Figure 2, Tables 4 and 5), the 1-chroma-1,3-diene unit of this compound is twisted and exhibits features similar to those of compound (*Z*)-**3b**, exept for the configuration of the C=C bond.

Binuclear 1-Metalla-1,3-dienes. Since bridged binuclear complexes containing *π* systems have gained much interest recently,[14,26–29] we have prepared the binuclear carbene complexes $(CO)_5M=C(OEt)CH=C(Ph)OArO(Ph)C=CH(OEt)C=M(CO)_5$ (M = Cr, W) by

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(25) Aumann, R.; Jasper, B.; Goddard, R.; Krüger, C. *Chem. Ber.* **1994**, *127*, 717–724.

(26) For a recent review see: Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem.* **1993**, *105*, 969–996; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923–960.

Table 4. Details of the X-ray Crystal Structure Analyses of (*E*)-10d: Data Collection and Structure Solution[a]

formula	$C_{26}H_{18}CrO_7$
fw	494.40
cryst system	monoclinic
space group	$P2_1/n$ (No. 14)
a (Å)	6.365(1)
b (Å)	18.771(2)
c (Å)	19.804(1)
β (deg)	95.32(1)
V (Å^3)	2355.9(5)
diffractometer	Enraf-Nonius MACH3
temp (K)	223(2)
λ (Å)	0.710 73
Z	4
F(000)	1016
D_{calcd} (Mg/m^3)	1.394
μ (cm^{-1})	5.3
empirical abs corr (%)	93.4−99.7
θ_{max} (deg)	25.00
no. of data collcd	4547
no. of unique data	4150
R_{merge}	0.047
no. of obsd data ($\geq 2\sigma(I)$)	3063
no. of refined params	308
$R1$ ($\geq 2\sigma(I)$)	0.051
w$R2$ ($\geq 2\sigma(I)$)	0.161
goodness-of-fit on F^2	1.104
largest diff peak and hole (e Å^{-3})	0.66/−0.61

[a] Programs used: SHELXS-86, SHELXL-93, and SCHAKAL-92.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for (*E*)-10d

C(1)−C(5)	1.458(5)	C(3)−C(4)	1.493(6)
O(2)−C(3)	1.444(4)	C(5)−C(6)	1.342(5)
Cr−C(1)	2.046(4)	C(6)−O(7)	1.371(4)
C(1)−O(2)	1.322(4)	O(7)−C(8)	1.392(5)
O(2)−C(1)−C(5)	107.5(3)	C(1)−C(5)−C(6)	124.0(3)
O(2)−C(1)−Cr	131.5(3)	C(5)−C(6)−O(7)	123.3(3)
C(5)−C(1)−Cr	121.0(3)	C(5)−C(6)−C(61)	126.1(3)
C(1)−O(2)−C(3)	123.4(3)	O(7)−C(6)−C(61)	110.2(3)
O(2)−C(3)−C(4)	106.7(3)	C(6)−O(7)−C(8)	118.7(3)

base-catalyzed addition of dihydroxyaryl compounds Ar(OH)$_2$ (Ar = 1,4-phenylene, 1,3-phenylene, 1,1′-binaphthyl). Reaction of 2 equiv of **1a**,**b** with 1,1′-binaphthol (**11**) affords compounds **12**. Isomers (*E*,*E*)-**12a**,**b** are formed in yields of 88% (**12a**) and 85% (**12b**) (Scheme 6). According to ^{1}H NMR measurements, these compounds slowly rearrange in solution and produce mixtures of (*E*/*Z*)-**12** and (*Z*/*Z*)-**12**.

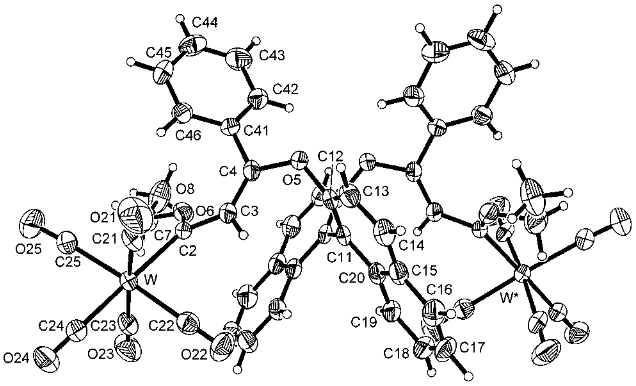
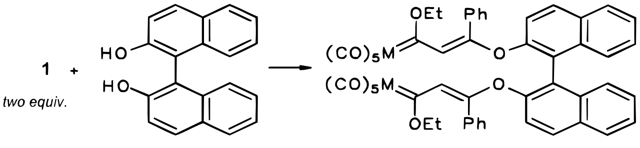


Figure 3. Molecular structure of binuclear compound (*E*,*E*)-**12a**.

Scheme 6. Binuclear 1-Metalla-1,3-dienes 12 Derived from 1,1′-Binaphthol



11

(*E*,*E*)- 12

Table 6. Crystal Data and Structure Analysis for (*E*,*E*)-12a

empirical formula	$C_{52}H_{34}O_{14}W_2 \cdot 2CH_2Cl_2$
fw	1420.34
temp (K)	223(2)
wavelength (Å)	0.710 73
cryst system	monoclinic
space group	$C2/c$ (No. 15)
a (Å)	27.503(1)
b (Å)	11.948(1)
c (Å)	17.166(1)
β (deg)	106.94(1)
V (Å^3)	5396.1(6)
Z	4
calcd density (Mg m^{-3})	1.748
F(000)	2760
μ (mm^{-1})	4.52
abs corr	ψ-scan
θ range (deg)	2.12−26.30
data collcd	5660
data indepd	5468
data obsd [$I \geq 2\sigma(I)$]	3597
refined params	361
R (all data/obsd)	0.069/0.029
wR^2 (all data/obsd)	0.118/0.091
diff Fourier (e Å^{-3})	1.18/−1.03
diffractometer	Enraf-Nonius MACH3
programs used	MolEN, SHELXS86, SHELXL-93, XP

The tungsten complex (*E*,*E*)-**12a** was characterized by X-ray analysis (Figure 3, Tables 6 and 7) of a crystal containing 2 molecules of CH$_2$Cl$_2$ per unit. A second sample of this compound, which has been obtained by recrystallizing from petroleum ether was also investigated. It was monoclinic, space group $P2_1/n$ (No. 14), with a = 17.338(2) Å, b = 9.665(1) Å, c = 32.168(3) Å, β = 102.28(1)°, V = 5267(1) Å^3, and Z = 4 at ambient temperature, and contained petroleum ether in a strongly disordered way, so that a convenient crystal chemical description of the solvent was not possible even with constraints. Refinement by neglecting the solvent and with anisotropic treatment of all non-hydrogen atoms (hydrogen atoms riding in calculated positions) lead to R = 0.055 for 613 parameters against 7097 independent reflections. Due to the missing part of electron density, the standard deviations were in the order of the second digit in the case of bond lengths. Therefore a detailed discussion of the structure of the hydrocarbon-containing sample could not be achieved. In this case the asymmetric unit contains one independent complete molecule with two metal centers, while in the crystals

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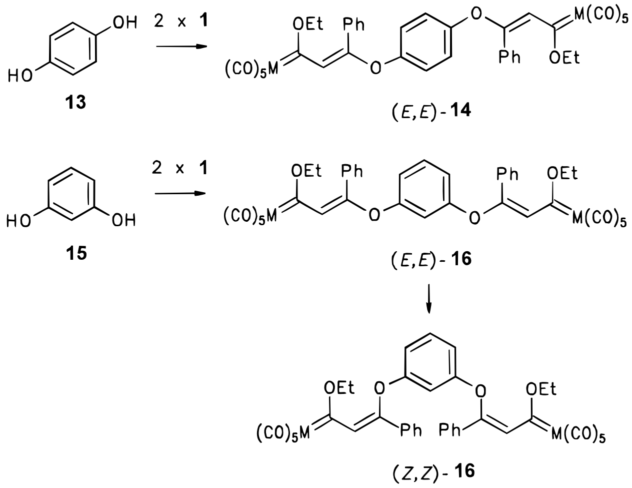
Table 7. Selected Bond Lengths (Å) and Angles (deg) for (*E*,*E*)-12a[a]

W−C(2)	2.201(5)	C(11)−C(11)^1	1.504(9)
C(2)−O(6)	1.308(6)	C(12)−C(13)	1.388(7)
C(2)−C(3)	1.445(6)	C(13)−C(14)	1.364(7)
C(3)−C(4)	1.341(6)	C(14)−C(15)	1.401(7)
C(4)−O(5)	1.369(5)	C(15)−C(16)	1.414(7)
O(5)−C(12)	1.401(5)	C(15)−C(20)	1.438(7)
O(6)−C(7)	1.434(6)	C(16)−C(17)	1.348(8)
C(7)−C(8)	1.476(8)	C(17)−C(18)	1.397(8)
C(11)−C(12)	1.374(6)	C(18)−C(19)	1.368(7)
C(11)−C(20)	1.432(6)	C(19)−C(20)	1.422(7)

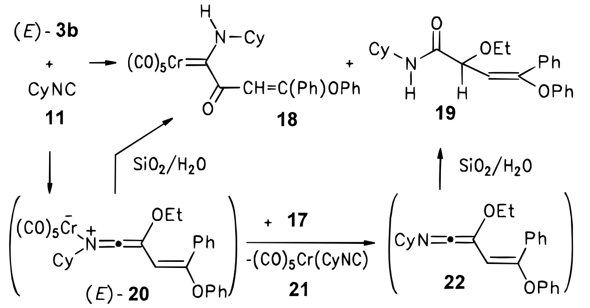
O(6)−C(2)−C(3)	108.0(4)	C(13)−C(12)−O(5)	115.3(4)
O(6)−C(2)−W	129.8(3)	C(14)−C(13)−C(12)	119.4(5)
C(3)−C(2)−W	122.2(4)	C(13)−C(14)−C(15)	121.3(5)
C(4)−C(3)−C(2)	126.3(5)	C(14)−C(15)−C(16)	122.7(5)
C(3)−C(4)−O(5)	123.4(4)	C(14)−C(15)−C(20)	118.8(5)
C(4)−O(5)−C(12)	119.4(4)	C(16)−C(15)−C(20)	118.5(5)
C(2)−O(6)−C(7)	123.5(4)	C(17)−C(16)−C(15)	121.8(5)
O(6)−C(7)−C(8)	107.5(5)	C(16)−C(17)−C(18)	120.2(5)
C(12)−C(11)−C(20)	117.5(4)	C(19)−C(18)−C(17)	120.9(6)
C(12)−C(11)−C(11)^1	120.9(4)	C(18)−C(19)−C(20)	120.8(5)
C(20)−C(11)−C(11)^1	121.6(4)	C(19)−C(20)−C(11)	122.7(5)
C(11)−C(12)−C(13)	123.5(5)	C(19)−C(20)−C(15)	117.8(4)
C(11)−C(12)−O(5)	121.1(4)	C(11)−C(20)−C(15)	119.4(4)

[a] Symmetry transformation used to generate equivalent atoms: (1) $-x$, y, $-z + {}^1/_2$.

Scheme 7. Binuclear 1-Metalla-1,3-dienes 14 and 16



Scheme 8. (Amino)ketocarbene Complex 18 and Acid Amide 19



containing dichloromethane, which data are reported in Tables 6 and 7, the molecule is built up by symmetry from one-half; *i.e.*, it contained only one metal center in the asymmetric unit. Nevertheless, comparision of both molecules in the two different structures shows no differences within the observed accuracy.

Bridged Binuclear Carbene Complexes 14 and 16 were derived from dihydroxyphenylenes **13** and **15** in 76−90%. While compounds (*E*,*E*)-**14a**,**b** prove to be configurationally quite stable, compound (*E*,*E*)-**16**, which is formed by kinetic reaction control, exhibits a strong tendency to form the isomer (*Z*,*Z*)-**16** in solution.

Ketenimine Derivatives from Metalladiene 10b. Ligand disengagement from Fischer carbene complexes can be most easily achieved by addition of isocyanides. The key step of this reaction involves insertion of the isocyano function into the M=C bond of the carbene complex, which leads to production of a ketenimine complex.[4b] Addition of cyclohexyl isocyanide (**17**) to the 1-chroma-1,3-diene (*E*)-**10b** seems to follow this general route to a ketenimine complex (*E*)-**20**. Depending on the reaction condition, a small portion of (*E*)-**20** undergoes a ligand exchange of the ketenimine against an isocyanide ligand. Thus, workup of the reaction mixture by chromatography affords compounds **18** and **19**, which are expected to be formed by hydrolysis of (*E*)-**20**, and **15**, respectively (Scheme 8).

Experimental Section

All operations were carried out under an atmosphere of argon. All solvents were dried and distilled prior to use. Hexane (bp 70 °C) was distilled and stored over sodium wire prior to use. All ^{1}H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra were recorded on a Bruker ARX 300 instrument in CDCl$_3$, unless otherwise indicated, and all chemical shift values refer to $\delta_{TMS} = 0.00$. ^{13}C NMR multiplicities were determined by DEPT measurements. NOE, double resonance spin-decoupling, and low-temperature ^{1}H NMR measurements were carried out on a Bruker AM 360 instrument. IR spectra were recorded on a Biorad digilab division FTS-45 FT-IR spectrophotometer. GC/IR spectra were recorded on a Shimadzu GC-14A gas chromatograph coupled to a Biorad digilab division GC/C32. GC analyses were conducted on a Shimadzu GC-14A. Elemental analysis were determined on a Perkin-Elmer 240 elemental analyzer. Analytical TLC plates, Merck DC-Alufolien Kieselgel 60$_{F240}$, were viewed by UV light (254 nm) and stained by a 5% aqueous acidic ammonium molybdate solution. R_f values refer to TLC tests. Chromatographic purifications were performed on Merck Kieselgel 100. Petroleum ether refers to that fraction boiling between 40 and 60 °C.

(3*Z*)-2-Ethoxy-4-[(3-oxocyclopent-1-enyl)oxy]-4-phenyl-1,1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadiene (3a) and Pentacarbonyl[9-oxo-4-phenyl-5,6-cyclopenteno-2*H*-pyran-2-ylidene]tungsten (4a). To pentacarbonyl(1-ethoxy-3-phenyl-2-propyne-1-ylidene)tungsten (**1a**) (482 mg, 1.00 mmol) and cyclopentane-1,3-dione (**2a**) (118 mg, 1.20 mmol) in 1 mL of dichloromethane in a 5-mL screwtop vessel is *slowly* added triethylamine (20 mg, 0.20 mmol) in 2 mL of dichloromethane with *vigorous stirring* at 20 °C. Reaction progress is followed by TLC. After the starting material has been consumed completely (*ca*. 1 h at 20 °C), solvent is removed in vacuo and the residue is dissolved in toluene. Chromatography on silica gel with dichloromethane affords blue **4a** (203 mg, 38%, R_f = 0.5 in 1:1 pentane/dichloromethane, blue crystals from 1:3 dichloromethane/pentane, mp 157 °C), and elution with dichloromethane/diethyl ether (5:1) yields a red fraction with **3a** (325 mg, 56%, R_f = 0.5 in dichloromethane, dark-red crystals from 1:6 dichloromethane/pentane at −15 °C, mp 173 °C).

3a. ^{1}H NMR (C$_6$D$_6$): δ 7.48 (1 H, s, 3-H), 7.32 and 6.95 (2:3 H, m each, Ph), 5.20 (1 H, s, OC=CH), 4.41 (2 H, q, OCH$_2$), 2.09 and 2.01 (2 H each, m each, CH$_2$ each), 0.94 (3 H, t, CH$_2$C*H*$_3$); ^{13}C NMR (C$_6$D$_6$): δ 305.5 (W=C), 203.9 and 197.5 [*trans*- and *cis*-CO, W(CO)$_5$], 202.0 and 186.0 (Cq each, C=O and =CO), 144.6 (Cq, C4), 132.7 (Cq, *i*-C Ph), 131.6 (CH, C3); 131.4, 129.5, and 126.9 (1:2:2, CH each, Ph), 109.6 (OC=*C*H), 80.1 (OCH$_2$), 34.7 and 27.5 (CH$_2$ each), 14.5 (CH$_2$*C*H$_3$). IR (diffuse reflection) (cm^{-1}): 2066.2, 1981.7, 1916.6 [ν(C$\equiv$O)], 1706.1 [ν(C=O)]. IR (hexane): 2067.7 (30), 1978.5 (5), 1941.3 (100) [ν(C$\equiv$O)]. MS (70 eV) [*m/e* (%)]: ^{184}W, 580 (20) [M$^+$], 552 (5), 524 (5), 496 (30), 468 (30), 440 (40) [M$^+$ − 5CO], 105 (100). Anal. Calcd for $C_{21}H_{16}O_8W$ (580.2): C, 43.47; H, 2.78. Found: C, 43.62; H, 2.54.

4a. ^{1}H NMR (C_6D_6): δ 7.98 (1 H, s, 3-H), 7.44 and 7.03 (2:3 H, m each, Ph), 1.82 and 1.70 (2 H each, m each, CH$_2$ each). ^{13}C NMR (C_6D_6): δ 263.5 (W=C), 204.3 and 198.7 [*trans*- and *cis*-CO, W(CO)$_5$], 196.2 and 192.8 (Cq each, C=O and C6), 142.7 (Cq, C4), 142.0 (CH, C3), 133.3 (Cq, *i*-C Ph); 131.8, 130.0, and 128.7 (1:2:2, CH each, Ph), 120.9 (Cq, C5), 33.9 and 25.4 (CH$_2$ each). IR (diffuse reflection) (cm^{-1}): 2060.9 (50), 1979.3 (10), 1913.1 (100) [ν(C$\equiv$O)], 1722.0 (30) [ν(C=O)]. Anal. Calcd for $C_{19}H_{10}O_7W$ (534.1): C, 42.73; H, 1.89. Found: C, 42.56; H, 1.81.

(3*Z*)-2-Ethoxy-4-[(3-oxocyclopent-1-enyl)oxy]-4-phenyl-1,1,1,1-pentacarbonyl-1-chroma-1,3-butadiene (3b) and Pentacarbonyl[9-oxo-4-phenyl-5,6-cyclopenteno-2*H*-pyran-2-ylidene]chromium (4b). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyne-1-ylidene)chromium (**1b**) (350 mg, 1.00 mmol) and cyclopentane-1,3-dione (**2a**) (118 mg, 1.20 mmol) in 1 mL of dichloromethane are reacted with triethylamine (20 mg, 0.20 mmol) as described above for 2 h at 20 °C. Chromatography on silica gel with dichloromethane affords blue **4a** (141 mg, 35%, $R_f = 0.5$ in 1:1 pentane/dichloromethane, blue crystals from 1:3 dichloromethane/pentane, mp 132 °C), and with dichloromethane/diethyl ether (5:1) a red fraction with **3a** is obtained (242 mg, 54%, $R_f = 0.5$ in dichloromethane, dark-red crystals from 1:6 dichloromethane/pentane at −15 °C, mp 162 °C).

3b. ^{1}H NMR (C_6D_6): δ 7.40 (1 H, s, 3-H), 7.30 and 7.05 (2:3 H, m each, Ph), 5.30 (1 H, s, OC=CH), 4.72 (2 H, q, OCH$_2$), 2.20 and 2.05 (2 H each, m each, CH$_2$ each), 1.05 (3 H, t, CH$_2$C*H*$_3$). ^{13}C NMR (C_6D_6): δ 334.9 (Cr=C), 224.5 and 217.0 [*trans*- and *cis*-CO, Cr(CO)$_5$], 202.2 and 186.4 (Cq each, C=O and =CO), 141.6 (Cq, C4), 132.8 (Cq, *i*-C Ph), 131.0 (CH, C3); 129.8, 127.5, and 126.7 (2:1:2, CH each, Ph), 110.2 (OC=*C*H), 77.7 (OCH$_2$), 35.0 and 27.9 (CH$_2$ each), 15.0 (CH$_2$*C*H$_3$). IR (diffuse reflection) (cm^{-1}): 2059.1, 1982.3, 1939.0 [ν(C$\equiv$O)], 1705.9 [ν(C=O)]. IR (hexane): 2059.8 (30), 1949.7 (100) [ν(C$\equiv$O)]. MS (70 eV) [*m/e* (%)]: 448 (20) [M$^+$], 308 (40) [M$^+$ − 5CO], 52 (100). Anal. Calcd for $C_{21}H_{16}CrO_8$ (448.4): C, 56.26; H, 3.60. Found: C, 56.16; H, 3.54.

4b. ^{1}H NMR (C_6D_6): δ 7.82 (1 H, s, 3-H), 7.24 and 6.85 (2:3 H, m each, Ph), 1.70 and 1.61 (2 H each, m each, CH$_2$ each). ^{13}C NMR (C_6D_6): δ 290.8 (Cr=C), 224.5 and 217.5 [*trans*- and *cis*-CO, Cr(CO)$_5$], 196.2 and 193.6 (Cq each, C=O and C6), 139.3 (CH, C3), 139.0 (Cq, C4), 132.0 (Cq, *i*-C Ph); 131.7, 130.4, and 129.1 (1:2:2, CH each, Ph), 120.5 (Cq, C5), 34.0 and 25.4 (CH$_2$ each). IR (diffuse reflection) (cm^{-1}): 2053.5, 1984.3, 1925.1 [ν(C$\equiv$O)], 1721.8 [ν(C=O)]. IR (hexane): 2055.4 (30), 1988.1 (5), 1952.0 (100) [ν(C$\equiv$O)]. MS (70 eV) [*m/e* (%)]: 402 (40) [M$^+$], 374 (10), 346 (20), 318 (40), 290 (40), 262 (40) [M$^+$ − 5CO], 52 (100). Anal. Calcd for $C_{19}H_{10}CrO_7$ (402.3): C, 56.76; H, 2.51. Found: C, 56.56; H, 2.46.

(3*Z*)-2-Ethoxy-4-[(5,5-dimethyl-3-oxocyclohex-1-enyl)oxy]-4-phenyl-1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadiene (3c) and Pentacarbonyl(7,7-dimethyl-4-phenyl-6,8-dihydro-2*H*-chromene-5-one-2-ylidene)tungsten (4c). To pentacarbonyl(1-ethoxy-3-phenyl-2-propyne-1-ylidene)tungsten (**1a**) (482 mg, 1.00 mmol) and 5,5-dimethylcyclohexane-1,3-dione (**2b**) (150 mg, 1.00 mmol) in a 5-mL screw-top vessel is added a solution of triethylamine (101 mg, 1.00 mmol) in 2 mL of diethyl ether. The mixture is shaken immediately for 3 min to give a violet precipitate in a slightly exothermic reaction. Pentane (2 mL) is added after 5 min at 20 °C, and the mixture is homogenized by ultrasonic irradiation for 10 min. According to a TLC, starting material is consumed completely. Centrifugation affords violet crystals of **4c** (299 mg, 52%, $R_f = 0.7$ in dichloromethane, mp 159 °C from 1:1 diethyl ether/pentane). Compound **3c** is accumulated in the mother liquor and can be isolated by fractionating crystallization (236 mg, 38%, brown crystals, mp 83 °C).

3c. ^{1}H NMR (C_6D_6): δ 7.44 (1 H, s, 3-H), 7.34 and 6.95 (2:3 H, m each, Ph), 5.49 (1 H, t, ^4J = 1 Hz, OC=CH), 4.50 (2 H, q, OCH$_2$), 2.08 (2 H, d, ^4J = 1 Hz, CH$_2$), 1.92 (2 H, s, CH$_2$), 1.08 (3 H, t, CH$_2$C*H*$_3$), 0.80 [6 H, s, C(CH$_3$)$_2$]. ^{13}C NMR (C_6D_6): δ 306.1 (W=C), 203.7 and 197.5 [*trans*- and *cis*-CO, W(CO)$_5$], 196.0 and 171.8 (Cq each, C=O and =CO), 144.5 and 144.0 (Cq each, C4 and *i*-C Ph), 132.7 (CH, C3); 131.1, 129.4, and 126.8 (1:2:2, CH each, Ph), 107.2 (Cq, C4a), 80.0 (OCH$_2$), 50.6 (Cq, *C*Me$_2$), 41.9 and 32.3 (CH$_2$ each, C6 and C8), 28.0 [C(*C*H$_3$)$_2$], 14.7 (CH$_2$*C*H$_3$). IR (diffuse reflection) (cm^{-1}): 2066.2, 1981.7, 1916.6 [ν(C$\equiv$O)], 1706.1 [ν(C=O)]. IR (hexane): 2067.3 (30), 1978.o (5), 1941.1 (100) [ν(C$\equiv$O)]. Anal. Calcd for $C_{24}H_{22}O_8W$ (622.3): C, 46.32; H, 3.56. Found: C, 46.38; H, 3.70.

4c. ^{1}H NMR (CDCl$_3$): δ 7.98 (1 H, s, 3-H), 7.50 (3 H, m, *m*- und *p*-H, C$_6$H$_5$), 7.31 (2 H, m, *o*-H, C$_6$H$_5$), 3.20 (2 H, s, 5-CH$_2$), 2.44 (2 H, s, COCH$_2$), 1.29 [6 H, s, (CH$_3$)$_2$]. ^{13}C NMR (CDCl$_3$): δ 262.4 (W=C), 204.5 and 198.2 [1:4, *trans*- and *cis*-CO, W(CO)$_5$], 193.8 (Cq, C=O), 181.4 (Cq, C6), 144.9 (CH, C3), 143.6 (Cq, C4), 135.4 (Cq, *i*-C, C$_6$H$_5$), 130.5−128.4 (CH, C$_6$H$_5$), 128.0 (Cq, C5), 52.7 (CO*C*H$_2$), 43.5 (6-CH$_2$), 32.4 [*C*(CH$_3$)$_2$)], 28.5 [C(*C*H$_3$)$_2$]. IR (diffuse reflection) (cm^{-1}): 2062.9, 1971.6, 1929.3, and 1890.5 [ν(C$\equiv$O)], 1698.0 [ν(C=O)], 1587.5 [ν(C=C)]. MS (70 eV) [*m/e* (%)]: 576 (20) [M$^+$], 436 (20) [M$^+$ − 5CO], 252 (15), 57 (100) [ligand$^+$]. Anal. Calcd for $C_{22}H_{16}O_7W$ (576.2): C, 45.86; H, 2.80. Found: C, 45.91; H, 2.67.

3-(1-Ethoxy-3-oxo-3-phenylpropenyl)cyclopent-2-enone (*Z*/*E*-5). (3*Z*)-1,1,1,1-Pentacarbonyl-2-ethoxy-4-(1-oxycyclopenten-3-one)-4-phenyl-1-chroma-1,3-butadiene (**3b**) (112 mg, 0.25 mmol) in 1 mL of C$_6$D$_6$ is heated for 2 h at 80 °C. According to TLC, the starting material has been consumed completely. A white precipitate of Cr(CO)$_6$ is formed, which is removed by centrifugation. The solution is analyzed spectroscopically. Addition of pentane affords a yellowish oil, consisting of a 3:1 mixture of *E*/*Z* stereoisomers of **5**, from which white crystals of (*E*)-**5a** are obtained after several days at 0 °C.

(*E*)-5. ^{1}H NMR (C_6D_6): δ 7.90, 7.19, and 7.05 (2:1:2 H, m each, Ph), 6.39 (1 H, t, ^4J = 1.7 and 1.7 Hz, 2′-H), 5.70 (1 H, s, 2-H), 3.20 (2 H, q, OCH$_2$), 2.51 (2 H, m, 4′-H$_2$), 2.10 (2 H, 5′-H$_2$), 0.95 (3 H, t, CH$_2$C*H*$_3$). ^{13}C NMR (C_6D_6): δ 207.2 (Cq, C3′), 189.0 (Cq, C3), 169.4 and 164.8 (Cq each, C1 and C1′), 139.8 (Cq, *i*-C, Ph); 134.0, 131.0, 128.4, and 128.2 (2:1:2:1, CH each, C2′ and Ph), 100.2 (CH, C2), 64.1 (OCH$_2$), 34.9 and 29.8 (CH$_2$ each, C4′ and C5′), 16.0 (CH$_3$). IR (diffuse reflection) (cm^{-1}): 1707.9 and 1858.8 [ν(C=O) each]. MS (70 eV) [*m/e* (%)]: 256 (20) [M$^+$], 228 (60) [M$^+$ − C$_2$H$_4$], 200 (40), 199 (50), 184 (60), 105 (80), 77 (100). Anal. Calcd for $C_{16}H_{16}O_3$ (256.3): C, 74.98; H, 6.29. Found: C, 75.16; H, 6.46.

(*Z*)-5. ^{1}H NMR (C_6D_6): δ 7.96, 7.02, and 6.94 (2:1:2 H, m each, Ph), 6.52 (1 H, t, ^4J = 1.7 and 1.7 Hz, 2′-H), 5.94 (1 H, s, 2-H), 3.90 (2 H, q, OCH$_2$), 1.98 (2 H, m, 4′-H$_2$), 1.82 (2 H, 5′-H$_2$), 0.93 (3 H, t, CH$_2$C*H*$_3$). ^{13}C NMR (C_6D_6): δ 206.8 (Cq, C3′), 190.1 (Cq, C3), 168.2 and 162.9 (Cq each, C1 and C1′), 139.0 (Cq, *i*-C, Ph); 132.9, 131.0, 128.6, and 128.0 (2:1:1:2:1, CH each, C2′ and Ph), 106.4 (CH, C2), 70.0 (OCH$_2$), 35.0 and 26.6 (CH$_2$ each, C4′ and C5′), 16.7 (CH$_3$). IR (diffuse reflection) (cm^{-1}): 1707.9 and 1858.8 [ν(C=O) each]. MS (70 eV) [*m/e* (%)]: 256 (20) [M$^+$], 228 (60) [M$^+$ − C$_2$H$_4$], 200 (40), 199 (50), 184 (60), 105 (80), 77 (100).

2-Ethoxy-4-(9-phenanthroxy)-4-phenyl-1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadiene [(*E*/*Z*)-7] and Pentacarbonyl(4-phenyl-2*H*-1-oxatriphenylen-2-ylidene)tungsten (8). To pentacarbonyl(1-ethoxy-3-phenyl-2-propyne-1-ylidene)tungsten (**1a**) (241 mg, 0.50 mmol) and 9-phenanthrol (**6**) (97 mg, 0.50 mmol) in a 5-mL screw-top vessel is added a solution of triethylamine (0.51 mg, 0.50 mmol) in 2 mL of diethyl ether. The mixture is shaken immediately for 3 min to give a dark red solution initially, from which a dark brown solid begins to precipitate in a *slightly* exothermic reaction.

According to TLC (in 4:1 pentane/dichloromethane) starting material ($R_f = 0.8$) is consumed completely after 3–4 min. Pentane (2 mL) is added to the mother liquor after 5 min at 20 °C, and the solid (*ca.* 280 mg) is removed by centrifugation after 10 min. Extraction with 5 mL of diethyl ether at 20 °C leaves a violet residue of compound **8** (84 mg, 28%, mp 60 °C). Concentration of the ether extract to 1 mL and addition of 3 mL of pentane affords essentially clean compound (*E*)-**7** (196 mg, 58%, $R_f = 0.6$ in 4:1 pentane/dichloromethane, mp 110 °C). A TLC of the mother liquor indicates the presence of bright-brown (*Z*)-**7** ($R_f = 0.7$ in 4:1 pentane/dichloromethane), together with traces of dark-brown (*E*)-**7** ($R_f = 0.6$) and of some violet compound **8** ($R_f = 0.5$). Compound (*Z*)-**7** is generated by thermal isomerization of (*E*)-**7** and is accumulated in the mother liquor from which it can be isolated by fractionating crystallization at −78 °C (52 mg, 15%, mp 81 °C). Thermal isomerization of either (*E*)-**7** or (*Z*)-**7** at 50 °C affords an isomer mixture of (*E*/*Z*) = 1:3.

(*E*)-7. ^{1}H NMR (C_6D_6): δ 8.43, 8.38, 8.16, and 7.60 (1 H each, m each, 1′-, 4′-, 5′-, and 8′-H, phenanth); 8.12 (1 H, s, 3-H), 7.52 and 7.03 (2:3 H, m each, 4-Ph); 7.41, 7.38, 7.35, and 7.18 (1 H each, m each, 2′-, 3′-, 6′-, and 7′-H, phenanth); 7.08 (1 H, s, 10′-H, phenanth), 4.23 (2 H, q, OCH_2), 0.56 (3 H, t, CH_3). ^{13}C NMR (C_6D_6): δ 301.6 (W=C), 203.7 and 197.8 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 159.6 (Cq, C-9, phenanth), 148.3 (Cq, C4), 135.6 (Cq, *i*-C, 4-Ph), 130.1, 129.8, and 128.2 (2:2:1, CH each, 4-Ph); 130.2–123.5 (CH each, C3, C-2′–C-4′ and C-5′–C-8′, phenanth), 131.3, 131.0, 126.5, and 124.3 (Cq each, C-10a′, C-4a′, C-4b′ and C-8a′, phenanth); 117.6 (CH, C-10′, phenanth), 78.6 (OCH_2), 13.6 (CH_3). IR (hexane) (cm^{-1}) (%): ν = 2064.7 (30), 1982.8 (5), 1940.2 (100) [ν(C≡O)]; 1553.6 (20) [ν(C=C)]. MS (70 eV), ^{184}W [*m*/*e* (%)]: 676 (20) [M$^+$], 648 (20), 620 (5), 592 (40), 536 (40) [M$^+$ − 5CO], 478 (50), 352 (40), 289 (60), 69 (100). Anal. Calcd for $C_{30}H_{20}O_7W$ (676.3): C, 53.28; H, 2.98. Found: C, 53.20; H, 3.10.

(*Z*)-7. ^{1}H NMR (C_6D_6): δ 8.43, 8.41, 8.30, and 7.40 (1 H each, "d" each, 1′-, 4′-, 5′-, and 8′-H, phenanth); 7.95 (1 H, s, 3-H), 7.70 and 6.88 (2:3 H, m each, 4-Ph); 7.45, 7.43, 7.25, and 7.21 (1 H each, "t" each, 2′-, 3′-, 6′-, and 7′-H, phenanth); 7.02 (1 H, s, 10′-H, phenanth), 4.10 (2 H, q, OCH_2), 0.43 (3 H, t, CH_3). ^{13}C NMR (C_6D_6): δ 303.9 (W=C), 203.7 and 197.8 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 151.5 (Cq, C-9, phenanth), 147.6 (Cq, C4), 134.2 (Cq, *i*-C, 4-Ph); 132.3, 131.4, 125.5, and 122.7 (Cq each, C-10a′, C-4a′, C-4b′, and C-8a′, phenanth); 132.2 (CH, C3); 130.9, 129.5, and 128.1 (2:2:1, CH each, 4-Ph); 132.1–122.6 (8 CH, C-2′–C-4′ and C-5′–C-8′, phenanth); 107.5 (CH, C-10′, phenanth), 80.0 (OCH_2), 14.0 (CH_3). IR (hexane) (cm^{-1}) (%): ν = 2065.3 (30), 1979.2 (5), 1941.4 (100) [ν(C≡O)]; 1554.4 (20) [ν(C=C)]. MS (70 eV), ^{184}W [*m*/*e* (%)]: 676 (10) [M$^+$], 648 (30), 620 (0), 592 (80), 536 (80) [M$^+$ − 5CO], 449 (90), 352 (90), 294 (100), 266 (95). Anal. Calcd for $C_{30}H_{20}O_7W$ (676.3): C, 53.28; H, 2.98. Found: C, 53.16; H, 3.05.

8. ^{1}H NMR ($CDCl_3$): δ 9.18, 8.86, 7.96 and 7.60 (1 H each, "d" each, 1′-, 4′-, 5′-, and 8′-H, phenanth); 8.28 (1 H, s, 3-H); 8.00, 7.92, 7.65, and 7.21 (1 H each, "d" each, 2′-, 3′-, 6′-, and 7′-H, phenanth), 7.53 (5 H, m, 4-Ph). ^{13}C NMR ($CDCl_3$): δ 254.6 (W=C), 204.1 and 198.4 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 162.8 (Cq, C-9′, phenanth), 144.5 (Cq, C4), 143.9 (CH, C3), 138.9 (Cq, *i*-C, C_6H_5); 132.5, 126.4, 123.3, and 116.6 (Cq each, C-10a′, C-4a′, C-4b′ and C-8a′, phenanth); 131.4, 129.7, 129.3, 129.2, 128.4, 127.9, 127.8, 127.7, 127.6, 127.3, 123.9, 123.2, 122.8 (CH each; C-2′–C-4′ and C-5′–C-8′, phenanth; diastereotopic C-2″–C-6″ 4-Ph). IR (hexane) (cm^{-1}): 2060.0 (30), 1933.8 (100) [ν(C≡O)]. MS (70 eV) [*m*/*e* (%)]: 630 (20) [M$^+$], 602 (10), 546 (60), 490 (100) [M$^+$ − 5CO], 462 (40), 434 (30). Anal. Calcd for $C_{28}H_{14}O_6W$ (630.3): C, 53.36; H, 2.24. Found: C, 53.64; H, 2.46.

2-Ethoxy-4-phenyl-4-phenoxy-1,1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadiene [(*E*)-10a and (*Z*)-10a]. To pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1a**) (482 mg, 1.00 mmol) and phenol (**9a**) (94 mg, 1.00 mmol) in 0.3 mL of diethyl ether in a 5-mL airtight screw-top vessel is added triethylamine (50 mg, 0.50 mmol) in 3 mL of pentane with stirring at 0 °C. A gradual change of color from brown to red is observed, and formation of a red compound **10a** can be followed by TLC ($R_f = 0.5$ in pentane). Starting material is consumed completely after 3–4 h at 0 °C, while a 10:1 mixture of (*E*/*Z*)-**10a** is formed initially (^{1}H NMR analysis in C_6D_6 at 10 °C). Bright red crystals of (*E*)-**10a** (mp 75 °C) are obtained by crystallization at −15 °C. Workup by chromatography on silica gel (20 × 2 cm column) with pentane/dichloromethane (5:1 to 3:1) affords a red fraction of isomer ratio (*E*/*Z*)-**10a** = 1:3 (^{1}H NMR analysis) (404 mg, 91%, red oil). An identical isomer ratio (*E*/*Z*)-**10a** = 1:3 is achieved in a solution of isomerically pure (*E*)-**10a** at 50 °C after 3 h. Fractionating crystallization of the (*E*/*Z*)-**10a** = 1:3 mixture from pentane at −15 °C affords dark red crystals of (*Z*)-**10a**, mp 75 °C.

(*E*)-10a. ^{1}H NMR (C_6D_6): δ 7.26 and 7.03 (2:3 H, m each, 4-Ph), 6.90, 6.75, and 6.65 (2:2:1 H, m each, 4-phenoxy), 7.08 (1 H, s, 3-H), 4.36 (2 H, q, OCH_2), 0.55 (3 H, t, CH_3). ^{13}C NMR (C_6D_6): δ 300.7 (W=C), 203.9 and 198.0 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 161.0 (Cq, *i*-C, phenoxy), 154.0 (C4), 135.8 (Cq, *i*-C, 4-Ph), 130.4 (CH, C3); 130.3, 129.6, and 128.1 (2:2:1, CH each, 4-Ph); 129.2, 121.4, and 115.7 (2:1:2, CH each, phenoxy); 78.6 (OCH_2), 13.6 (CH_3). IR (hexane) (cm^{-1}) (%): ν = 2064.7 (30), 1982.8 (5), 1942.2 (100) [ν(C≡O)]; 1552.8 (20) [ν(C=C)]. MS (70 eV), ^{184}W [*m*/*e* (%)]: 576 (20) [M$^+$], 548 (30), 492 (60), 464 (40), 436 (70) [M$^+$ − 5CO], 377 (100), 351 (95), 324 (100). Anal. Calcd for $C_{22}H_{16}O_7W$ (576.2): C, 45.86; H, 2.80. Found: C, 45.66; H, 2.73.

(*Z*)-10a. ^{1}H NMR (C_6D_6): δ 7.65 (1 H, s, 3-H), 7.53 and 6.90 (2:3 H, m each, 4-Ph); 6.90, 6.75, and 6.66 (2:2:1 H, m each, 4-phenoxy), 4.32 (2 H, q, OCH_2), 0.83 (3 H, t, CH_3). ^{13}C NMR (C_6D_6): δ 303.8 (W=C), 203.8 and 197.9 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 157.7 (Cq, *i*-C, phenoxy), 148.5 (C4), 134.4 (Cq, *i*-C, 4-Ph), 131.2 (CH, C3); 130.9, 129.6, and 128.1 (2:2:1, CH each, 4-Ph); 129.0, 122.7, and 116.3 (2:1:2, CH each, phenoxy); 79.7 (OCH_2), 14.3 (CH_3). IR (hexane) (cm^{-1}) (%): ν = 2064.8 (30), 1982.9 (5), 1943.5 (100) [ν(C≡O)]; 1558.9 (20) [ν(C=C)]. MS (70 eV), ^{184}W [*m*/*e* (%)]: 576 (10) [M$^+$], 548 (20), 492 (60), 464 (50), 436 (80) [M$^+$ − 5CO], 377 (100). Anal. Calcd for $C_{22}H_{16}O_7W$ (576.2): C, 45.86; H, 2.80. Found: C, 45.91; H, 2.62.

2-Ethoxy-4-phenyl-4-phenoxy-1,1,1,1,1-pentacarbonyl-1-chroma-1,3-butadiene [(*Z*)-10b and (*E*)-10b]. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)chromium (**1b**) (482 mg, 1.00 mmol) and phenol (**9a**) (94 mg, 1.00 mmol) are reacted as described above for 3–4 h at 0 °C to afford an (*E*/*Z*) = 10:1 mixture of **10b**, which is isomerized to an (*E*/*Z*) = 3:2 mixture at 50 °C for 3 h. Chromatography on silica gel yields an (*E*/*Z*) = 3:2 mixture (466, 81%, red oil). Fractionating crystallization from pentane at −15 °C yields dark red crystals of (*Z*)-**10b**, mp 74 °C, and bright red crystals of (*E*)-**10b**, mp 87 °C.

(*E*)-10b. ^{1}H NMR (C_6D_6): δ 7.29 and 7.05 (2:3 H, m each, 4-Ph), 7.09, 6.92, and 6.88 (2:2:1 H, m each, 4-phenoxy), 7.07 (1 H, s, 3-H), 4.36 (2 H, q, OCH_2), 0.55 (3 H, t, CH_3). ^{13}C NMR (C_6D_6): δ 328.5 (Cr=C), 224.2 and 217.4 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 157.8 (Cq, *i*-C, phenoxy), 154.1 (C4), 135.7 (Cq, *i*-C, 4-Ph), 130.1 (CH, C3); 129.8, 128.6, and 126.5 (2:2:1, CH each, 4-Ph); 129.0, 121.7, and 116.1 (2:1:2, CH each, phenoxy); 76.0 (OCH_2), 14.2 (CH_3). IR (hexane) (cm^{-1}) (%): ν = 2056.0 (30), 1943.7 (100) [ν(C≡O)]; 1551.5 (20) [ν(C=C)]. MS (70 eV) [*m*/*e* (%)]: 444 (10) [M$^+$], 416 (10), 388 (5) 360 (60), 332 (30), 304 (60) [M$^+$ − 5CO], 276 (60), 275 (40), 260 (60), 145 (80), 52 (100). Anal. Calcd for $C_{22}H_{16}CrO_7$ (444.4): C, 59.47; H, 3.63. Found: C, 59.64; H, 3.66.

(*Z*)-10b. ^{1}H NMR (C_6D_6): δ 7.68 (1 H, s, 3-H), 7.53 and 6.90 (2:3 H, m each, 4-Ph); 6.88, 6.79, and 6.67 (2:2:1 H, m each, 4-phenoxy), 4.49 (2 H, q, OCH_2), 0.87 (3 H, t, CH_3). ^{13}C NMR (C_6D_6): δ 331.5 (Cr=C), 224.4 and 217.2 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 157.0 (Cq, *i*-C, phenoxy), 144.9 (C4), 134.3 (Cq, *i*-C, 4-Ph), 131.1 (CH, C3); 130.2, 128.4, and 127.9 (2:2:1, CH each, 4-Ph); 129.4, 123.2, and 116.8 (2:1:2, CH each, phenoxy); 77.2 (OCH$_2$), 14.6 (CH$_3$). IR (hexane) (cm^{-1}) (%): ν = 2056.5 (30), 1979.9 (5), 1945.8 (100) [ν(C≡O)]; 1558.5 (20) [ν(C=C)]. MS (70 eV) [*m/e* (%)]: 444 (20) [M$^+$], 416 (30), 388 (20) 360 (40), 332 (30), 304 (30) [M$^+$ − 5CO], 276 (50), 145 (80), 52 (100). Anal. Calcd for $C_{22}H_{16}CrO_7$ (444.4): C, 59.47; H, 3.63. Found: C, 59.66; H, 3.54.

2-Ethoxy-4-(naphthalen-2-yloxy)-4-phenyl-1,1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadiene [(*Z*)-10c and (*E*)-10c]. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1a**) (482 mg, 1.00 mmol) and 2-naphthol (**9b**) (144 mg, 1.00 mmol) are reacted as described above. A dark brown solution is obtained initially from which brick red crystals of (*E*)-**10c** begin to precipitate at 20 °C after 30 min (bright red crystals from diethyl ether/pentane at −15 °C). Starting material is consumed completely after 3−4 h at 20 °C, while an 8:1 mixture of (*E*/*Z*)-**10c** is formed (^{1}H NMR analysis at 10 °C). At 50 °C after 3 h a 2:5 mixture of (*E*/*Z*)-**10c** is obtained, from which (*Z*)-**10c** is isolated by fractional crystallization at −15 °C (black needles). Workup by chromatography on silica gel (20 × 2 cm column) with pentane/dichloromethane (5:1 to 3:1) affords a red fraction with an (*E*/*Z*) = 2:5 mixture of **10c** (R_f = 0.5, 5:1 pentane/dichloromethane, total yield 532 mg, 85%).

(*E*)-10c. ^{1}H NMR (C$_6$D$_6$): δ 7.53 (3 H, m, napht), 7.38 and 7.03 (2:3 H, m each, 4-Ph); 7.20 and 7.10 (3:1 H, m each, napht), 7.07 (1 H, s, 3-H), 4.22 (2 H, q, OCH$_2$), 0.53 (3 H, t, CH$_3$). ^{13}C NMR (C$_6$D$_6$): δ 300.7 (W=C), 203.9 and 197.9 [1:4, *trans*- and *cis*-CO, W(CO)$_5$], 160.8 (Cq, C2′), 151.4 (C4); 135.8, 134.5, and 129.9 (Cq each; C9′, C10′, and *i*-C 4-Ph), 130.9 (CH, C3); 129.3, 128.0, and 127.8 (2:2:1, CH each, 4-Ph); 128.7, 128.1, 127.2, 126.0, 125.9, 120.4, and 118.2 (CH each, C4′, C5′, C7′, C8′, C6′, C3′, C1′), 78.2 (OCH$_2$), 13.2 (CH$_3$). IR (hexane) (cm^{-1}) (%): ν = 2064.4 (30), 1982.2 (5), 1941.2 (100) [ν(C≡O)]; 1548.4 (20) [ν(C=C)]. MS (70 eV), ^{184}W [*m/e* (%)]: 626 (20) [M$^+$], 598 (60), 542 (60), 414 (40), 486 (70) [M$^+$ − 5CO], 429 (100). Anal. Calcd for $C_{26}H_{18}O_7W$ (626.3): C, 49.86; H, 2.90. Found: C, 48.99; H, 2.93.

(*Z*)-10c. ^{1}H NMR (C$_6$D$_6$): δ 7.76 (1 H, s, 3-H), 7.49 (3 H, m, napht), 7.64 and 6.83 (2:3 H, m each, 4-Ph); 7.45, 3.39, and 7.35 (1 H each, d each, 4′-H, 5′-H, and 8′-H), 7.19 (1 H, d, 1′-H), 7.10−7.00 (3 H, m, 3′-H, 6′-H, and 7′-H), 4.18 (2 H, q, OCH$_2$), 0.74 (3 H, t, CH$_3$). ^{13}C NMR (C$_6$D$_6$): δ 304.1 (W=C), 203.0 and 197.2 [1:4, *trans*- and *cis*-CO, W(CO)$_5$], 155.2 (Cq, C2′), 148.3 (C4); 134.5, 134.3, and 129.2 (Cq each; C9′, C10′, and *i*-C 4-Ph), 131.2 (CH, C3); 130.7, 128.5, and 127.4 (2:2:1, CH each, 4-Ph); 128.5, 128.3, 127.9, 127.1, 124.9, 117.8, and 111.5 (CH each, C4′, C5′, C7′, C8′, C6′, C3′, C1′), 79.7 (OCH$_2$), 14.3 (CH$_3$). IR (hexane) (cm^{-1}) (%): ν = 2064.2 (30), 1981.9 (5), 1940.3 (100) [ν(C≡O)]; 1557.2 (20) [ν(C=C)]. MS (70 eV), ^{184}W [*m/e* (%)]: 626 (20) [M$^+$], 598 (60), 542 (60), 414 (30), 486 (70) [M$^+$ − 5CO], 427 (100). Anal. Calcd for $C_{26}H_{18}O_7W$ (626.3): C, 49.86; H, 2.90. Found: C, 48.89; H, 3.03.

2-Ethoxy-4-(naphthalen-2-yloxy)-4-phenyl-1,1,1,1,1-pentacarbonyl-1-chroma-1,3-butadiene [(*Z*)-10d and (*E*)-10d]. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)chromium (**1b**) (350 mg, 1.00 mmol) and 2-naphthol (**9a**) (144 mg, 1.00 mmol) are reacted as described above. After 3−4 h at 20 °C a 6:1 mixture of (*E*/*Z*)-**10d** is formed (^{1}H NMR analysis at 10 °C). (*E*)-**10d** is isolated by fractionating crystallization at −15 °C as brick-red crystals, mp 89 °C. At 50 °C after 3 h an (*E*/*Z*) = 2:3 mixture is obtained, from which (*Z*)-**10d** is isolated by fractionating crystallization at −15 °C (black needles, mp 96 °C). Workup by (rapid) chromatography on silica gel (20 × 2 cm column) with pentane/dichloromethane (5:1 to 3:1) affords a red fraction with an (*E*/*Z*) = 2:3 mixture of **10d** (R_f = 0.5, 5:1 pentane/dichloromethane, total yield 430 mg, 87%).

(*Z*)-10d. ^{1}H NMR (C$_6$D$_6$): δ 7.74 (1 H, s, 3-H), 7.60 and 6.90 (2:3 H, m each, 4-Ph); 7.45, 7.40, 7.21, 7.14, and 7.08 (1:2:1:2:1 H, m each, napht), 4.42 (2 H, q, OCH$_2$), 0.80 (3 H, t, CH$_3$). ^{13}C NMR (C$_6$D$_6$): δ 332.1 (Cr=C), 224.7 and 217.5 [1:4, *trans*- and *cis*-CO, Cr(CO)$_5$], 155.3 (Cq, C2′), 144.4 (C4); 134.6, 134.2, and 130.3 (Cq each; C9′, C10′, and *i*-C 4-Ph), 130.9 (CH, C3); 129.4, 128.7, and 128.5 (2:1:1, CH each, 4-Ph); 129.9, 128.6, 127.2, 127.1, 124.9, 117.8, and 111.6 (CH each, C4′, C5′, C7′, C8′, C6′, C3′, C1′), 77.5 (OCH$_2$), 15.0 (CH$_3$). IR (hexane) (cm^{-1}) (%): ν = 2056.7 (30), 1979.9 (5), 1946.0 (100) [ν(C≡O)]; 1559.0 (20) [ν(C=C)]. MS (70 eV) [*m/e* (%)]: 494 (20) [M$^+$], 466 (30), 438 (10) 410 (40), 372 (30), 354 (30) [M$^+$ − 5CO], 326 (50), 310 (40), 52 (100). Anal. Calcd for $C_{26}H_{18}CrO_7$ (494.4): C, 63.16; H, 3.67. Found: C, 63.32; H, 3.52.

(*E*)-10d. ^{1}H NMR (C$_6$D$_6$): δ 7.60 (3 H, m, napht), 7.30 (1 H, d, 1′-H), 7.20 and 7.10 (2:3 H, m each, 4-Ph); 7.15 (4 H, m, napht), 7.07 (1 H, s, 3-H), 4.32 (2 H, q, OCH$_2$), 0.56 (3 H, t, CH$_3$). ^{13}C NMR (C$_6$D$_6$): δ 328.6 (Cr=C), 224.2 and 217.1 [1:4, *trans*- and *cis*-CO, Cr(CO)$_5$], 157.2 (Cq, C2′), 151.7 (C4); 135.6, 131.6, and 130.3 (Cq each; C9′, C10′, and *i*-C 4-Ph), 130.7 (CH, C3); 130.1, 128.3, and 128.0 (2:2:1, CH each, 4-Ph); 128.5, 128.1, 127.2, 126.1, 125.4, 120.6, and 118.3 (CH each, C4′, C5′, C7′, C8′, C6′, C3′, C1′), 76.0 (OCH$_2$), 13.8 (CH$_3$). IR (hexane) (cm^{-1}) (%): ν = 2056.7 (30), 1979.9 (5), 1946.0 (100) [ν(C≡O)]; 1552.2 (20) [ν(C=C)]. Anal. Calcd for $C_{26}H_{18}CrO_7$ (494.4): C, 63.16; H, 3.67. Found: C, 63.09; H, 3.66.

2,2′-Bis(2-ethoxy-4-phenyl-1,1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadien-4-yloxy)-1,1′-binaphthalenyl [(*E*,*E*)-12a]. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1a**) (482 mg, 1.00 mmol) and 1,1′-binaphth-2-ol (**11**) (143 mg, 0.50 mmol) are reacted as described above. Fractionating crystallization affords brick-red crystals of (*E*,*E*)-**12a** (R_f = 0.4, 5:1 pentane/dichloromethane, 434 mg, 88%). ^{1}H NMR (C$_6$D$_6$): δ 7.65 and 7.38 (1:1 H, d each, ^3J = 9 Hz, 3′-H and 4′H), 7.51 and 7.45 (1:1 H, dd each, ^3J = 6.5 and 2 Hz each, 5′-H and 8′-H), 7.22 and 7.16 (1:1 H, t each, 6′-H and 7′-H), 6.93 (1 H, s, 3-H), 6.88 and 6.82 (2:3 H, m each, 4-Ph), 3.92 and 3.87 (1 H each, m each, diastereotopic OCH$_2$), 0.26 (3 H, t, CH$_3$). ^{13}C NMR (C$_6$D$_6$): δ 300.4 (W=C), 203.7 and 197.9 [1:4, *trans*- and *cis*-CO, W(CO)$_5$], 160.7 (Cq, C2′), 152.1 (C4); 135.8, 134.3, 132.2, and 129.8 (Cq each; C9′, C10′, C2′, and *i*-C 4-Ph), 129.9 (CH, C3); 129.3, 128.0, and 127.7 (2:2:1, CH each, 4-Ph); 128.6, 128.1, 127.1, 126.0, 125.9, and 120.2 (CH each, C4′, C5′, C7′, C8′, C6′, C3′), 78.0 (OCH$_2$), 13.3 (CH$_3$). IR (hexane) (cm^{-1}) (%): ν = 2064.6 (20), 1983.2 (5), 1941.8 (100) [ν(C≡O)]; 1548.5 (20) [ν(C=C)]. Anal. Calcd for $C_{52}H_{34}O_{14}W_2$ (1250.5): C, 49.94; H, 2.74. Found: C, 49.92; H, 2.81.

2,2′-Bis(2-ethoxy-4-phenyl-1,1,1,1,1-pentacarbonyl-1-chroma-1,3-butadien-4-yloxy)-1,1′-binaphthalenyl [(*E*,*E*)-12b]. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)chromium (**1b**) (350 mg, 1.00 mmol) and 1,1′-binaphth-2-ol (**11**) (143 mg, 0.50 mmol) are reacted as described above. After 3−4 h at 20 °C the starting material is consumed completely. Fractionating crystallization at −15 °C affords brick-red crystals of (*E*,*E*)-**12b** (R_f = 0.4, 5:1 pentane/dichloromethane, 419 mg, 85%). ^{1}H NMR (C$_6$D$_6$): δ 7.65 and 7.42 (1:1 H, d each, ^3J = 9 Hz, 3′-H and 4′H), 7.50 and 7.42 (1:1 H, dd each, ^3J = 6.5 and 2 Hz each, 5′-H and 8′-H), 7.20 and 7.15 (1:1 H, t each, 6′-H and 7′-H), 6.99 (1 H, s, 3-H), 6.95 and 6.85 (2:3 H, m each, 4-Ph), 3.90 (2 H, m, diastereotopic OCH$_2$), 0.28 (3 H, t, CH$_3$). ^{13}C NMR (C$_6$D$_6$): δ 328.7 (Cr=C), 224.1 and 217.4 [1:4, *trans*- and *cis*-CO, Cr(CO)$_5$], 156.3 (Cq, C2′), 150.3 (C4); 135.6, 134.0, and 131.2 (Cq each, C9′, C10′, and *i*-C 4-Ph); 131.2 (CH, C3); 129.8, 128.7, and 128.5 (2:2:1, CH each, 4-Ph); 130.7, 129.0, 127.8, 127.1, 125.3 (CH each; C4′, C5′, C6′, C7′, C8′); 123.7 (Cq, C1′), 121.7 (CH, C3′), 75.8 (OCH$_2$), 13.5 (CH$_3$). IR (hexane) (cm^{-1}) (%): ν = 2056.4 (30), 1979.8 (5), 1945.1 (100) [ν(C≡O)]; 1553.0 (20) [ν(C=C)]. Anal. Calcd for $C_{52}H_{34}Cr_2O_{14}$ (986.8): C, 63.29; H, 3.47. Found: C, 63.45; H, 3.64.

***μ*-(1,4-Phenylene)bis[(2-ethoxy-4-phenyl-1,1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadien-4-yl)oxy] [(*E*,*E*)-14a].** To pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1a**) (482 mg, 1.00 mmol) and 1,4-dihydroxybenzene (**13**) (55 mg, 0.50 mmol) in 2.5 mL of diethyl ether in a 5-mL airtight screw-top vessel is added triethylamine (50 mg, 0.50 mmol) in 1.5 mL of pentane with stirring at 20 °C. While stirring is continued, brick red crystals are formed, which are removed by centrifugation after 15 h at 20 °C. (*E*,*E*)-**14a** is obtained (R_f = 0.5, 3:1 pentane/dichloromethane, total yield 480 mg, 89%). ^{1}H NMR (C_6D_6): δ 7.28 and 7.05 (4:6 H, m each, 2 4-Ph), 7.03 (2 H, s, 2 3-H), 6.81 (4 H, s, 1,4-phenylene), 4.23 (4 H, q, OCH_2), 0.55 (6 H, t, CH_3). ^{13}C NMR ($CDCl_3$): δ 302.3 (W=C), 204.0 and 197.9 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 159.5 (Cq, *i*-C, 1,4-phenylene), 151.7 (C4), 135.5 (Cq, *i*-C, 4-Ph), 131.5 (CH, C3); 130.4, 129.4, and 128.1 (2:2:1, CH each, 4-Ph), 118.2 (CH, 1,4-phenylene), 78.8 (OCH_2), 14.1 (CH_3). IR (hexane) (cm^{-1}) (%): $\nu = 2064.6$ (30), 1982.6 (5), 1942.0 (100) [ν(C≡O)]; 1553.5 (20) [ν(C=C)]. Anal. Calcd for $C_{38}H_{26}O_{14}W_2$ (1074.3): C, 42.48; H, 2.44. Found: C, 42.42; H, 2.57.

***μ*-(1,4-Phenylene)bis[(2-ethoxy-4-phenyl-1,1,1,1,1-pentacarbonyl-1-chroma-1,3-butadien-4-yl)oxy] [(*E*,*E*)-14b].** Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)chromium (**1b**) (385 mg, 1.00 mmol) and 1,4-dihydroxybenzene (**13**) (55 mg, 0.50 mmol) in 2.5 mL of diethyl ether is reacted as described above to give (*E*,*E*)-**14b** ($R_f = 0.5$, 3:1 pentane/dichloromethane, total yield 308 mg, 76%). ^{1}H NMR (C_6D_6): δ 7.30 and 6.95 (4:6 H, m each, 2 4-Ph), 7.02 (2 H, s, 2 3-H), 6.80 (4 H, s, 1,4-phenylene), 4.32 (4 H, q, OCH_2), 0.55 (6 H, t, CH_3). ^{13}C NMR ($CDCl_3$): δ 328.3 (Cr=C), 224.0 and 216.7 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 158.5 (Cq, *i*-C, 1,4-phenylene), 151.5 (C4), 134.9 (Cq, *i*-C, 4-Ph), 129.9 (CH, C3); 129.0, 128.9, and 128.0 (2:2:1, CH each, 4-Ph), 122.6 (CH, 1,4-phenylene), 75.8 (OCH_2), 13.9 (CH_3). IR (hexane) (cm^{-1}) (%): $\nu = 2058.5$ (30), 1938.1 (100) [ν(C≡O)]; 1554.3 (20) [ν(C=C)]. Anal. Calcd for $C_{38}H_{26}Cr_2O_{14}$ (810.6): C, 56.31; H, 3.23. Found: C, 56.42; H, 3.56.

***μ*-(1,3-Phenylene)bis[(2-ethoxy-4-phenyl-1,1,1,1,1-pentacarbonyl-1-chroma-1,3-butadien-4-yl)oxy] [(*E*,*E*)-16b and (*Z*,*Z*)-16b].** Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)chromium (**1b**) (385 mg, 1.00 mmol) and 1,3-dihydroxybenzene (**15**) (55 mg, 0.50 mmol) in 2.5 mL of diethyl ether is reacted as described above to give an 8:1 mixture of **16b** (^{1}H NMR analysis at 10 °C), from which (*E*,*E*)-**16b** is isolated by fractionating crystallization at −15 °C as brick-red crystals. Workup by (rapid) chromatography on silica gel (20 × 2 cm column) with pentane/dichloromethane (5:1 to 3:1) affords a red fraction of an isomer mixture of **16b** ($R_f = 0.5$, 4:1 pentane/dichloromethane, total yield 365 mg, 90%). After 16 h at 20 °C the isomer ratio has changed to (*E*,*E*/*Z*,*Z*)-**16b** = 1:5. Crystallization at −15 °C affords (*Z*,*Z*)-**16b** (black crystals, mp 116 °C).

(*E*,*E*)-16b. ^{1}H NMR (C_6D_6): δ 7.30 and 6.98 (4:6 H, m each, 2 4-Ph), 7.08 (2 H, s, 2 3-H); 6.90, 6.83, and 6.70 (1:1:2 H; t, "s", "d"; 1,3-phenylene), 4.35 (4 H, q, OCH_2), 0.52 (6 H, t, CH_3). IR (hexane) (cm^{-1}) (%): $\nu = 2058.5$ (30), 1938.1 (100) [ν(C≡O)]; 1554.3 (20) [ν(C=C)]. Anal. Calcd for $C_{38}H_{26}Cr_2O_{14}$ (810.6): C, 56.31; H, 3.23. Found: C, 56.35; H, 3.43.

(*Z*,*Z*)-16b. ^{1}H NMR (C_6D_6): δ 7.52 (2 H, s, 2 3-H), 7.40 and 6.90 (4:6 H, m each, 2 4-Ph); 6.68, 6.46, and 6.40 (1:1:2 H; t, dd, dd; 1,3-phenylene), 4.48 (4 H, q, OCH_2), 0.80 (6 H, t, CH_3). ^{13}C NMR ($CDCl_3$): δ 332.4 (Cr=C), 224.2 and 217.0 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 158.4 (Cq, *i*-C, 1,3-phenylene), 143.1 (C4), 133.8 (Cq, *i*-C, 4-Ph), 130.7 (CH, C3); 129.5, 128.7, and 128.3 (2:1:2, CH each, 4-Ph), 111.2 and 105.5 (2:1 C, CH each, 1,3-phenylene), 77.0 (OCH_2), 14.6 (CH_3). IR (hexane) (cm^{-1}) (%): $\nu = 2057.1$ (30), 1946.6 (100) [ν(C≡O)]; 1561.0 (20) [ν(C=C)]. Anal. Calcd for $C_{38}H_{26}Cr_2O_{14}$ (810.6): C, 56.31; H, 3.23. Found: C, 56.45; H, 3.42.

Pentacarbonyl[1-(cyclohexylamino)-2-oxo-4-phenyl-4-phenoxybutenylidene]chromium (18) and 2-Ethoxy-*N*-cyclohexyl-1-oxo-4-phenoxy-4-phenyl-3-butenamide (19). To 2-ethoxy-4-phenyl-4-phenoxy-1,1,1,1,1-pentacarbonyl-1-chroma-1,3-butadiene (**10b**) (444 mg, 1.00 mmol) and water (18 mg, 1.00 mmol) in 1 mL of diethyl ether in a 5-mL airtight screw-top vessel is added cyclohexyl isocyanide (109 mg, 1.00 mmol) in 3 mL of diethyl ether dropwise with stirring at 0 °C. According to TLC starting material is consumed completely after a few minutes. Workup by chromatography on silica gel (20 × 2 cm column) with pentane/dichloromethane (1:1) affords an orange fraction of **18** ($R_f = 0.5$ in dichloromethane, 315 mg, 60%, orange crystals from dichloromethane/pentane (1:3) at −15 °C) and a colorless fraction with **19** ($R_f = 0.2$ in dichloromethane, 91 mg, 24%, colorless oil).

18. ^{1}H NMR (C_6D_6): δ 9.23 (1 H, s broad, NH); 7.23, 6.95 and 6.55 (2:2:1 H, m each, 4-Ph), 6.80 (5 H, m, 4-phenoxy), 7.02 (1 H, s, 3-H), 4.05 (1 H, m, NCH); 1.72, 1.63, 1.55, and 1.00 (2:2:1:5 H, m each, Cy). ^{13}C NMR (C_6D_6): δ 265.8 (Cr=C), 223.0 and 216.9 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 194.0 (Cq, C=O), 163.4 (Cq, *i*-C, phenoxy), 155.4 (C4), 133.1 (Cq, *i*-C, 4-Ph), 130.9 (CH, C3); 129.7, 128.7, and 128.0 (2:2:1, CH each, 4-Ph); 123.9, 118.5, and 112.4 (2:1:2, CH each, phenoxy); 62.6 (NCH); 31.9, 24.7, and 24.1 (2:1:2, CH_2 each). IR (diffuse reflection) (cm^{-1}) (%): $\nu = 2055.2$ (30), 1977.2 (10), 1950.4 (100) [ν(C≡O)]; 1587.2 (20) [ν(C=C)]. MS (70 eV) [*m*/*e* (%)]: 525 (5) [M^+], 497 (10), 441 (30), 413 (20), 385 (50) (60) [$M^+ - 5CO$], 94 (100). Anal. Calcd for $C_{27}H_{23}CrNO_7$ (525.5): C, 61.71; H, 4.41; N, 2.67. Found: C, 61.83; H, 4.62; N, 2.80.

19. ^{1}H NMR (C_6D_6): δ 7.50, 7.05, and 6.70 (2:2:1 H, m each, 4-Ph); 7.25 and 6.95 (2:3 H, m, 4-phenoxy), 6.85 (1 H, d broad, NH), 5.90 and 4.95 (1 H each, AB system, $^3J = 9.5$ Hz, 2-H and 3-H), 3.90 (1 H, m, NCH), 3.50 and 3.20 (1 H each, diastereotopic OCH_2); 2.05, 1.80, 1.45, 1.30, 1.23 (1:2:2:2:3 H, m each, Cy), 1.03 (3 H, t, CH_3). IR (diffuse reflection) (cm^{-1}) (%): $\nu = 3430$ (20) [ν(N−H)], 1677.9 and 1519.5 [δ(N−H)], 1593.1 [ν(C=C)].

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Supporting Information Available: Tables of data collection parameters, positional and displacement parameters, and bond distances and angles and SCHAKAL diagrams (37 pages). Ordering information is given on any current masthead page.

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