Organic Syntheses via Transition Metal Complexes. 72.[1] (2-(Acyloxy)ethenyl)carbene Complexes by Michael Addition of Carboxylic Acids to Alkynylcarbene Complexes (M = Cr, W). (2-(Acyloxy)ethenyl)ketene Imines by Ligand Disengagement with Isocyanide

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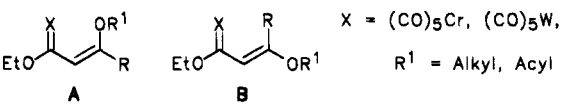
(2-(Acyloxy)ethenyl)carbene complexes $(CO)_5M{=}C(OEt){-}CH{=}C(OCOR)Ph$ [(*Z*)-**5**] (M = Cr, W; R = Ph, *p*-$Me_2NC_6H_4$, CH_3, *c*-$C_7H_7CH_2$, PhCH=CPh, $Me_2C{=}CH$, 1,4-C_6H_4) are obtained by the addition of carboxylic acids $R{-}CO_2H$ (**4**) to alkynylcarbene complexes $(CO)_5M{=}C(OEt){-}C{\equiv}CPh$ (**1**) (M = Cr, W) in the presence of Et_3N at 20 °C in 71–78% isolated yields. The reaction is regio- and stereochemically uniform. (*Z*)-**5g** (R = PhCH=CPh), $C_{31}H_{22}O_8W$, was characterized by X-ray diffraction. It crystallizes in space group $P\bar{1}$ with cell parameters a = 10.381(6) Å, b = 11.444(6) Å, c = 13.509(7) Å, α = 107.84(4)°, β = 91.54(4)°, γ = 108.49(4)°, Z = 2, R_1 = 0.0354, and wR_2 = 0.0811. Ligand disengagement from (*Z*)-**5** with *tert*-butyl isocyanide (**8b**) at 20 °C results in the formation of [2-(acyloxy)ethenyl]ketene imines *t*-$BuN{=}C{=}C(OEt){-}CH{=}C(OCOR)Ph$ [(*Z*)-**11**] (>95% yields).

Alkenylcarbene complexes $(CO)_5M{=}C{-}C{=}C$ of chromium and tungsten have gained much interest recently as C_3 building blocks for the synthesis of carbocyclic[2] and heterocyclic[3] rings. Though this class of compounds has been known since 1967,[4] systematic studies have been initiated only recently. Complexes $(CO)_5M{=}C{-}C{=}C(OR^1)$ of types **A** and **B** deserve particular attention due to their structural relationship to β-keto ester equivalents of the enol ether (R^1 = alkyl) and enol ester type (R^1 = acyl), respectively (Chart 1).

Chart 1



Enol Ethers 3

Complexes $(CO)_5M{=}C{-}C{=}C[O(alkyl)]$ (M = Cr, W) of the enol *ether* type are accessible by several methods (Scheme 1): (a) by the condensation of methylcarbene complexes $(CO)_5M{=}C(OEt)CH_3$ with dimethylformamide or other nonenolizable acid amides $R^1{-}CONR_2$ (eq 1),[5] (b) by the condensation of aryl- or alkylcarbene complexes with enolizable acid amides $R^1CH_2{-}CONR_2$, which involves the insertion of a CCN unit of the acid amide into the M=C bond (eq 2),[6] (c) by the insertion of alkynes into the M=C bond of alkoxycarbene complexes (eq 3),[5b,7,8] or (d) by the addition of alcohols to alkynylcarbene complexes (eq 4).[9–11] The latter reaction has been applied, e.g., to the introduction of carbohydrates as chiral inductors into alkenylcarbene complexes.[11] (b)–(d) usually yield (*E*)/(*Z*) mixtures of (2-alkoxyethenyl)carbene complexes, in which the (*E*) stereoisomers predominate (Scheme 1).

Enol Esters 5

Enol esters $(CO)_5M{=}C{-}C{=}C[O(acyl)]$ (**5**) (M = Cr, W) of types A and B are expected to react differently from

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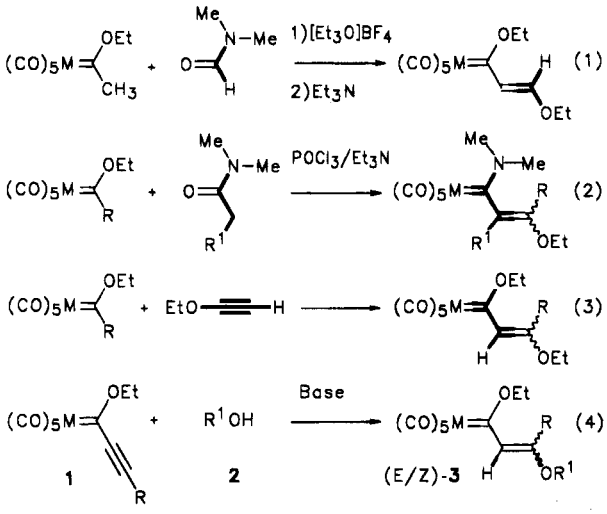
Scheme 1. Paths to (2-Alkoxyethenyl)carbene Complexes

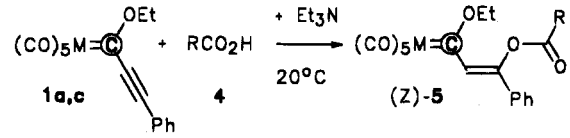


M = Cr, W; R = Alkyl, Aryl

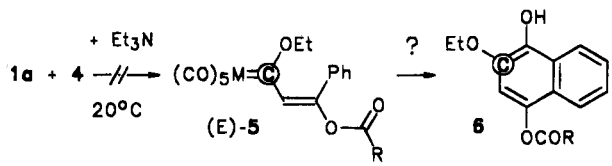
1-3	M	R	R^1	[3] %	(E/Z)-3	lit.
a	Cr	Ph	OEt	62	9	[9,10]
b	Cr	Ph	Oglucofuranosyl	90	4	[11]
c	W	Ph	Oglucofuranosyl	88	3	[11]
d	Cr	*c*Pr	OEt	77	100	[10]
e	Cr	CMe_2OEt	OEt	76	60	[10]

enol ethers $(CO)_5M{=}C{-}C{=}C[O(alkyl)]$ (**3**). The C=C-[O(alkyl)] group experiences an increase in electron density due to a π-conjugative interaction stronger than the C=C[O(acyl)] unit, in which the electron-withdrawing effect of the acylcarbonyl group plays the dominant role. An O-acylation usually leads to the destabilization of carbene complexes. This is especially true for compounds in which the acyl group is attached to the carbene carbon atom directly. It is well-known that (1-acyloxy)carbene complexes[12] $(CO)_5M{=}C(OCOR)R'$ (M = Cr, W) are by far less stable than 1-alkoxycarbene complexes $(CO)_5M{=}C(OR)R'$. The former are used *in situ* mostly, e.g., for the preparation of alkoxy-,[13a] imino-,[13b] or thiocarbene complexes[14] by nucleophilic 1-substitution reactions, or as precursors for the elimination of 1-alkenyl esters[15] from enolizable carbene ligands. (2-(Acyloxy)ethenyl)carbene complexes $(CO)_5M{=}C(OEt){-}CR{=}C(OCOR)R'$ prove to be more stable than (1-acyloxy)carbene complexes. We initiated studies on the reactivity of such compounds and describe here an efficient route to the preparation of these compounds as well as to their transformation into (2-(acyloxy)ethenyl)ketene imines **11**. Striking differences between enol ethers **3** and enol ethers **5** have been observed in their reactions with isocyanides.

Scheme 2. (2-(Acyloxy)ethenyl)carbene Complexes (*Z*)-5 by Addition of Carboxylic Acids 4 to Alkynylcarbene Complexes 1



4,5	M	R	5[%]	(Z/E)
a	Cr	C_6H_5	76	100
b	W	C_6H_5	78	100
c	W	p-Me_2N-C_6H_4	74	100
d	W	CH_3	73	100
e	W	c-C_7H_7-CH_2	71	100
f	W	$Me_2C{=}CH$	75	100
g	W	(E)-PhCH=CPh	74	100



(2-(Acyloxy)ethenyl)carbene Complexes 5

The addition of carboxylic acids to alkynes is an important method for the preparation of carboxylic acid 1-alkenyl esters.[16] In many cases it requires tough conditions and/or catalysts (acids,[17,18] mercury salts,[19] silver salts,[20] palladium salts,[21] or ruthenium complexes[22]). Though unsymmetrically substituted alkynes usually yield mixtures of regio- and stereoisomers,[16] the addition of carboxylic acids to the C≡C bond of alkynylcarbene complexes **1** proves to be regio- and stereochemically uniform. It is catalyzed by triethylamine under very mild conditions (20 °C, 2–20 h) and gives stable (2-(acyloxy)ethenyl)carbene complexes (*Z*)-**5** in 71–78% isolated yields (Scheme 2). The formation of isomers (*E*)-**5** has not been observed, nor that of 1,2,4-trioxynaphthalines **6**, which possibly could arise from cyclocarbonylation[23,24] of (*E*)-**5**.

Configuration of Enol Ethers 3 vs Enol Esters 5

The addition of carboxylic acids **4** and alcohols **2**, respectively, to the C≡C bond of alkynylcarbene complexes yields adducts of opposite stereochemistry. **4** forms enol *esters* **5** of (*Z*) configuration only, while **2**

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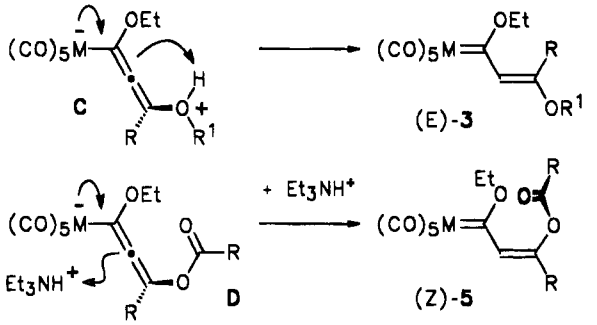
Scheme 3. Stereoselectivity Due to Different Protonation Sites in Zwitterionic and Anionic Intermediates, C and D, Respectively



gives enol *ethers* **3** of (*E*) configuration mainly. On the basis of earlier studies, an (*E*)/(*Z*) interconversion under the mild reaction conditions applied can be excluded for enol ethers **3**[9-11] as well as for enol esters **5**.[25] The opposite stereochemistry of the products should be kinetically controlled and may result from different protonation sites of the allene-type[11] intermediates **C** and **D** (Scheme 3). Due to the higher nucleophilicity of alcohols as compared to that of carboxylic acids, the former are expected to yield zwitterionic adducts **C** with **1** in the rate determining reaction step. A similar type reaction has been postulated on the basis of kinetic measurements on the addition of amines to **1**.[26] Carboxylic acids are far less reactive than alcohols toward the addition to **1**, but they are easily deprotonated by triethylamine and form carboxylates. The latter are expected to give anionic adducts of type **D** with **1**. Thus the stereodifferentiation may result from different modes of protonation of **C** and **D**. An intramolecular proton transfer of **C** should yield *syn* addition products (*E*)-**3** (Scheme 3), while an intermolecular protonation of **D**, which is directed by the structure of the ion pair, should lead to the formation of *anti* addition products (*Z*)-**5**.

5 displays chemical shifts within a narrow and characteristic range for 2-H (7.82-8.00 ppm) and OCH_2 (4.40–4.65 ppm) in the ^1H NMR and for C1 [(*Z*)-**5a**; 334 ppm; (*Z*)-**5b**–**k**, 305–307 ppm], C2 (132–134 ppm), and C3 (139–143 ppm) in the ^{13}C NMR spectra. Significant differences are observed between δ(C1) of the chromium (**5a**) and tungsten complexes (**5b**–**k**). The presence of a $(CO)_5M$ unit is indicated in the IR spectra by the [ν(C≡O)] bands [e.g.: (*Z*)-**5a** cm^{-1} (%) 2059.0 (30), 1986.3 (5), 1945.8 (100); (*Z*)-**5b** 2067.1 (30), 1982.4 (5), 1944.9 (100)], of which the frequencies of the A_1 bands play a guiding role in distinguishing between the chromium and tungsten complexes. The assignment of the (*Z*) configuration is based on NOE experiments, which indicate a positive interaction between 2-H and the *ortho* protons of the 3-Ph group. In order to obtain more structural details, a crystal structure analysis of (*Z*)-**5g** was performed.

Crystal Structure Analysis of (*Z*)-5g

Figure 1 shows the molecular structure and Tables 2 and 3 gives the experimental data for the crystal

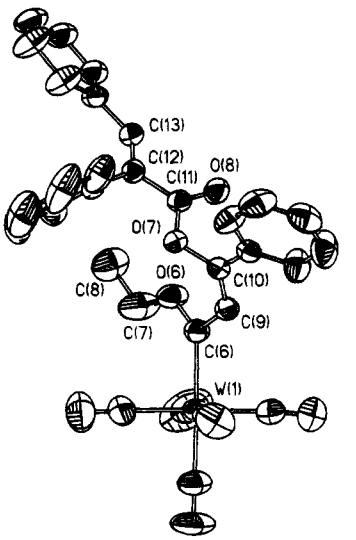


Figure 1. View of the molecular structure of (*Z*)-**5g** with selected bond distances (pm) and angles (deg) W(1)–C(6) 218.3(4), C(6)–O(6) 131.4(5), C(6)–C(9) 147.3(6), C(9)–C(10) 133.8(5), C(10)–O(7) 139.5(4), O(7)–C(11) 135.9(5), O(8)–C(11) 119.8(5); C(11)–C(12) 149.5(5); C(12)–C(13) 133.4(6); O(6)–C(6)–C(9) 108.5(4); O(6)–C(6)–W(1) 131.5(3).

Table 1. Selected ^{13}C (^1H) NMR Shifts[a] and IR Vibrations[b] of (2-(Acyloxy)ethenyl)ketene Imines

11	*C1*	*C2*	*HC3*	*C4*	OCH_2	*3-H*	OCH_2	ν(C=C=N)	ν(OC=O)
b	197.3	112.7	110.6	142.4	67.0	6.20	3.50	1994.9	1739.8
c	197.0	112.9	110.9	142.9	67.1	6.25	3.55	1985.5	1719.3
d	194.2	112.3	110.4	142.4	67.0	6.20	3.50	1987.8	1764.3
e	198.4	113.6	111.8	143.9	67.0	6.17	3.48	1986.4	1759.1

[a] In C_6D_6; chemical shifts in ppm relative to TMS, δ scale. [b] Diffuse reflection; [ν(C=C=N)] and [ν(OC=O)] vibrations in cm^{-1}.

structure of (*Z*)-**5g**. The plane defined by O6–C6–C9 at the carbene carbon atom approximately bisects the angle between two cisoid CO groups at the tungsten atom (C9–C6–W1–C1 121.5°). The double bond between C9–C10 is localized [C9–C10 133.8(5) pm] and within the expected range (see, e.g.: 1,3-butadiene, 133.0 pm for C1–C2). The carboxylic group is arranged almost perpendicular to the C9–C10 bond (C9–C10–O7–C11 −101.2°). Though a delocalization of electron density from O7 into the C=C bond should be possible from such a conformation, this is expected to be smaller than the delocalization from O6 into the W=C bond (C7–O6–O6–O9 179.5°) according to the shorter distance of O6–C6 131.4 pm as compared to O7–C10 139.5 pm. The C=C bond C9–C10 is arranged *s-trans* with respect to the W=C bond (W1–C6–C9–C10 −149.0°) and forms a 1-metalla 1,3-diene unit in an "open conformation".

(2-Alkoxyethenyl)- and (2-(Acyloxy)ethenyl)-ketene Imines

Common to enol ethers **3** and enol esters **5** is the ease by which the M=C bonds are transformed into C=C bonds by the insertion of an isocyanide. This type of reaction has been studied with a broad range of carbene complexes and seems to be of a very common type.[3b,c] Nevertheless, different products are obtained on reaction of isocyanides **8** with enol ethers **7** (Scheme 4) and enol ethers **5** (Scheme 5), respectively. The former, e.g.,

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Table 2. Crystal Data and Structure Refinement for (Z)-5g[a]

empirical formula	$C_{31}H_{22}O_8W$
fw	706.3
temp (K)	293(2)
wavelength (Å)	0.710 73
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	
a (Å)	10.381 (6)
b (Å)	11.444 (6)
c (Å)	13.509 (7)
α (deg)	107.84 (4)
β (deg)	91.54 (4)
γ (deg)	108.49 (4)
vol (Å^3)	1435.1
Z	2
density (calcd) (Mg/m^3)	1.635
abs coeff (mm^{-1})	4.07
F(000)	692
cryst size (mm)	0.22 × 0.25 × 0.32
θ range for data collcn (deg)	2.09−27.06
index ranges	$0 \le h \le 13, -14 \le k \le 13, -17 \le l \le 17$
no. of reflns collcd	6656
no. of ind reflns	6302 [R(int) = 0.0145]
refinement method	full-matrix least squares on F^2
Data/restraints/params	6300/0/361
goodness-of-fit on F^2	1.133
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0354$, $wR_2 = 0.0811$
R indices (all data)	$R_1 = 0.0407$, $wR_2 = 0.0841$
largest diff peak and hole (e Å^{-3})	+1.138 and −1.269

[a] Further details of the crystal structure (complete bond length and angles and displacement parameters) may be requested from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, FRG, on quoting the depository number CSD-57818, the name of the authors, and the journal citation.

the (2-alkoxyethenyl)carbene complex (*E*)-**7b**, inserts cyclohexyl isocyanide (**8a**) and yields a 4,5-dihydropyrrolylidene complex **9b** (probably *via* intermediates **E** and **F**, Scheme 4), in line with earlier observations on similar reactions with (*E*)-**7a**[27] and related compounds.[28]

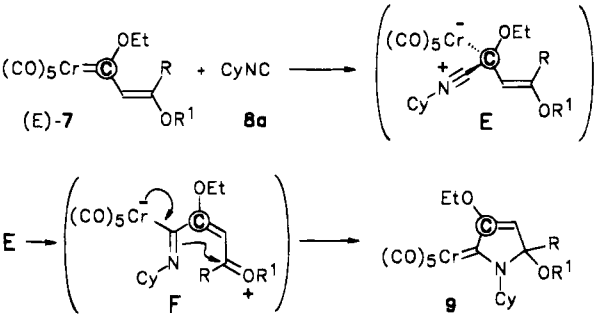
A quite different reaction takes place with enol *esters* (*Z*)-**5**. These add *2* equiv of *tert*-butyl isocyanide (**8b**) instead of 1 and give hitherto unknown[29] (2-(acyloxy)-ethenyl)ketene imines (*Z*)-**11** in essentially quantitative yields at 20 °C (Scheme 5). **8b** apparently reacts faster with (*Z*)-**10** than it does with (*Z*)-**5** and replaces (*Z*)-**11** by formation of an isocyanide complex **12**. A cyclization of (*Z*)-**10** to give 4,5-dihydropyrrolylidene complexes **13** (of type **9**) is not observed with enol *ester* (*Z*)-**5**. In contrast to (*Z*)-(2-(acylamino)ethenyl)ketene imines, which are obtained in a similar reaction from (*Z*)-(2-(acylamino)ethenyl)carbene complexes, and which undergo a spontaneous ring-closing metathesis at 20 °C with formation of pyrroles and isocyanates,[30] the (*Z*)-(2-(acyloxy)ethenyl)ketene imines do not produce furans in an analogous metathesis reaction, even at 90 °C (Scheme 5). The ketene imines (*Z*)-**11** on the other hand prove to be more sensitive to hydrolysis than the corresponding acylamino derivatives[30] on chromatography on silica gel and yield α-chiral acid amides **14** by addition of water (Scheme 5). The isolation of (*Z*)-**11** is possible by fractional crystallization, which of course involves a severe drop in yields. We therefore recommend to test mixtures of (*Z*)-**11** and **12** directly for further chemical transformations.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for (Z)-5g[a]

	x	y	z	U(eq)
W(1)	2099(1)	3034(1)	164(1)	47(1)
O(1)	−850(6)	2418(7)	−1010(5)	127(2)
O(2)	5113(5)	3606(6)	1193(4)	100(2)
O(3)	3259(6)	3034(5)	−1978(4)	107(2)
O(4)	2890(7)	6080(5)	618(6)	141(3)
O(5)	1653(5)	12(4)	−428(4)	91(1)
O(6)	490(4)	3612(4)	2152(3)	66(1)
O(7)	−686(3)	1640(3)	2843(2)	46(1)
O(8)	257(3)	3158(3)	4412(2)	57(1)
C(1)	200(6)	2636(6)	−579(4)	76(2)
C(2)	4022(5)	3399(5)	843(4)	64(1)
C(3)	2855(6)	3012(5)	−1214(4)	70(1)
C(4)	2572(7)	4983(6)	491(5)	80(2)
C(5)	1783(5)	1081(5)	−220(4)	60(1)
C(6)	1241(4)	2980(4)	1614(3)	48(1)
C(7)	151(9)	4616(8)	1858(6)	104(3)
C(8)	−872(7)	4966(6)	2445(6)	92(2)
C(9)	1405(4)	2050(4)	2115(3)	46(1)
C(10)	569(4)	1459(4)	2687(3)	40(1)
C(11)	−743(4)	2491(4)	3783(3)	41(1)
C(12)	−2181(4)	2441(4)	3923(3)	43(1)
C(13)	−2309(4)	3375(4)	4751(3)	46(1)
C(14)	777(4)	466(4)	3094(3)	44(1)
C(15)	−320(5)	−396(5)	3355(4)	65(1)
C(16)	−133(7)	−1327(6)	3735(5)	80(2)
C(17)	1123(7)	−1412(5)	3857(4)	76(2)
C(18)	2208(6)	−590(7)	3604(6)	90(2)
C(19)	2050(5)	364(6)	3229(5)	76(2)
C(20)	−3523(4)	3585(4)	5179(3)	50(1)
C(21)	−4787(6)	2595(5)	5017(5)	77(2)
C(22)	−5872(6)	2881(7)	5500(6)	90(2)
C(23)	−5712(6)	4122(6)	6129(5)	75(2)
C(24)	−4488(6)	5099(6)	6297(4)	70(1)
C(25)	−3393(5)	4831(5)	5837(4)	60(1)
C(26)	−3317(4)	1389(4)	3130(4)	54(1)
C(27)	−3935(5)	1671(6)	2358(4)	71(1)
C(28)	−4954(6)	680(9)	1601(6)	105(2)
C(29)	−5360(7)	−560(8)	1608(8)	119(3)
C(30)	−4788(6)	−858(6)	2381(8)	114(3)
C(31)	−3747(5)	117(5)	3150(6)	81(2)

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

Scheme 4. 4,5-Dihydropyrrolylidene Complexes 9 by Cyclization of (2-Alkoxyethenyl)carbene Complexes (*E*)-7 with 8a

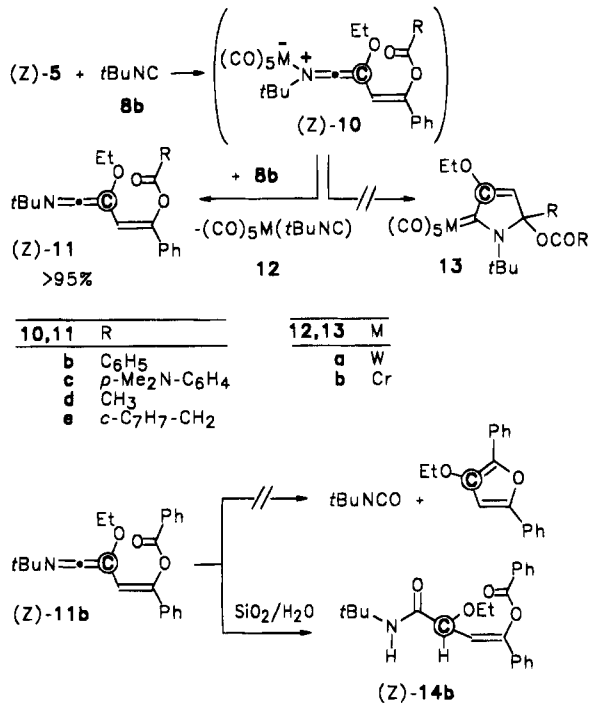


7, **9**: R = H, R^1 = Et (**a**); Ph, Me (**b**)

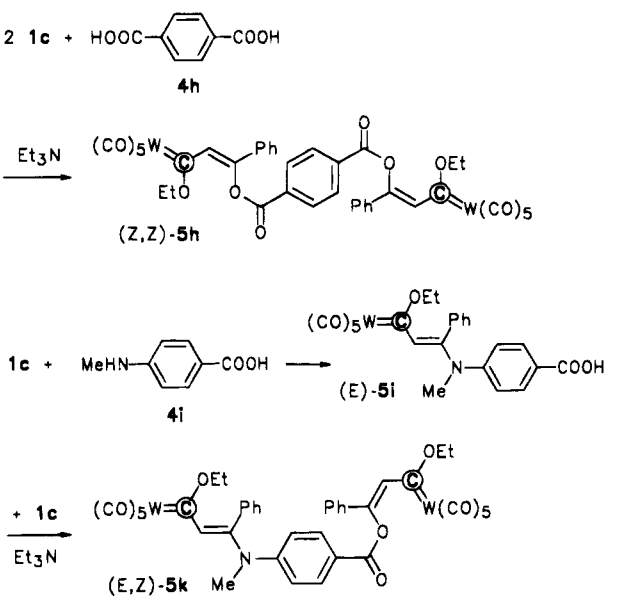
4,5-Dihydropyrrolidene complexes **9** show the spectroscopic characteristics of aminocarbene complexes [e.g. **9b**: NMR δ(Cr*C*) = 265.2 ppm, δ(*CH*N) = 5.25, δ(*C*HN) = 68.5; IR ν(C≡O): 2055.2 cm^{-1}, 1977.8, 1933.4]. Ketene imines (*Z*)-**11** are easily distinguished from **9** by the ^{13}C NMR signals of the central (δ 194.2−198.4 ppm) and terminal carbon atoms (δ 112.7−113.6) of the

(27) Aumann, R.; Hinterding, P. *Chem. Ber.* **1991**, *124*, 213−218.
(28) Aumann, R.; Heinen, H. *Chem. Ber.* **1986**, *119*, 3801−3811.
(29) Review: Perst, H. In Keten-imine. Methods of Organic Chemistry; Houben-Weyl, G. Thieme Verlag: Stuttgart, 1993, Vol. E15 III, pp 2531−2700.
(30) Aumann, R. *Chem. Ber.* **1994**, *127*, 717−724.

Scheme 5. (2-(Acyloxy)ethenyl)ketene Imines (*Z*)-11 by Ligand Disengagement from (2-(Acyloxy)ethenyl)carbene Complexes (*Z*)-5



Scheme 6. Bis(carbene) Complexes (*Z,Z*)-5h and (*E,Z*)-5k



NCC unit, as well as by the IR bands of ν(N=C=C) at 1985–1995 cm^{-1} and of ν(OC=O) at 1719–1764 cm^{-1} (Table 1).

(Bis)carbene Complexes 5h and 5k

The reaction shown in Scheme 2 can also be applied to the addition of dicarboxylic acid **4h** to **1c**, in which case a bridged bis(carbene) complex (*Z,Z*)-**5h** is obtained. By addition of an amino carboxylic acid **4i** to **1c** the (2-aminoethenyl)carbene complex (*E*)-**5i** is formed. This reacts with a further molecule of **1c** to give (*E,Z*)-**5k**, if Et_3N is added as a catalyst (Scheme 6). Thus, apparently, a bigger variety of bis(carbene) complexes is available from **1c** in high stereoselectivity.

Experimental Section

All operations were performed under argon. Solvents were dried by distillation from sodium/benzophenone, Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR, Bruker WM 300 (multiplicities were determined by DEPT; chemical shifts refer to $\delta_{TMS} = 0.00$ ppm); IR, Digilab FTS 45; MS, Finnigan MAT 312; elemental analysis, Perkin-Elmer 240 elemental analyzer; column chromatography, Merck-Kieselgel 100; TLC, Merck DC-Alufolien Kieselgel 60 F 254. R_f values refer to TLC tests.

[(2*Z*)-3-(Benzoyloxy)-1-ethoxy-3-phenyl-2-propenylidene]pentacarbonylchromium [(*Z*)-5a]. To 350 mg (1.00 mmol) of pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)-chromium (**1a**) and 121 mg (1.00 mmol) of benzoic acid (**4a**) in 3 mL of dichloromethane/diethyl ether (1:1) is added at 20 °C in a 5-mL airtight screw-top vessel with stirring 50 mg (0.50 mmol) of triethylamine. After a few minutes the formation of polar dark brown (*Z*)-**5a** can be detected by TLC ($R_f = 0.5$, pentane/dichloromethane 3:1). **1a** is completely consumed after 12–15 h at 20 °C. Workup by (rapid) chromatography on silica (column 20 × 2 cm) with pentane/dichloromethane (3:1) to (2:1). After a small yellow-orange fraction a dark brown fraction of (*Z*)-**5a** is obtained (360 mg, 76%, black crystals from diethyl ether/pentane (1:5), mp 83 °C). ^{1}H NMR (C_6D_6): δ 8.05, 7.15, and 7.00 (2:1:2, *o*-:*p*-:*m*-H, 3-benzoyloxy), 7.82 (1H, s, 2-H), 7.55, 6.90, 6.85 (2:1:2, *o*-:*p*-:*m*-H, 3-Ph), 4.55 (2H, q, OCH_2), 0.80 (3H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 334.2 (Cr=C), 224.7 and 217.1 [1:4, *trans*- and *cis*-CO, Cr-$(CO)_5$], 163.5 (O—CO), 139.4 (C3), 134.3 (*i*-C, 3-Ph), 134.1 (CH, 2-C), 129.8 (*i*-C, 3-benzoyloxy), 131.0, 130.6, 129.2 (1:2:2, *p*-:*o*-:*m*-CH, 3-benzoyloxy), 129.4, 128.4, 127.2 (2:1:2, *o*-:*p*-:*m*-CH, 3-Ph), 77.6 (OCH_2), 14.8 (CH_3). IR (hexane), cm^{-1} (%): 2059.0 (30), 1986.3 (5), 1945.8 (100) [ν(C≡O)]; (diffuse reflection) 1743.6 (20) [ν(OC=O)]. MS (70 eV), *m/e* (%): 472 (10) [M$^+$], 416 (10), 388 (5), 360 (50), 332 (50) [M$^+$ − 5CO], 289 (60), 288 (60), 275 (50), 260 (50), 251 (40), 220 (60), 173 (50), 129 (60), 105 (80), 51 (100). Anal. Calcd for $C_{23}H_{16}CrO_8$ (472.2): C, 58.48; H, 3.41. Found: C, 58.49; H, 3.52.

[(2*Z*)-3-(Benzoyloxy)-1-ethoxy-3-phenyl-2-propenylidene]pentacarbonyltungsten [(*Z*)-5b]. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1c**) (482 mg, 1.00 mmol) and 121 mg (1.00 mmol) of benzoic acid (**4a**) in 3 mL of dichloromethane/diethyl ether (1:1) are treated as described above with 80 mg (0.80 mmol) of triethylamine at 20 °C. Chromatography after 2–3 h yields (*Z*)-**5b**, $R_f = 0.4$ in pentane/dichloromethane (3:1) (470 mg, 78%, dark brown crystals from diethyl ether/pentane (1:6), mp 106 °C). ^{1}H NMR (C_6D_6): δ 8.00, 7.15, and 7.05 (2:1:2, *o*-:*p*-:*m*-H, 3-benzoyloxy), 7.92 (1H, s, 2-H), 7.55, 6.95, 6.85 (2:1:2, *o*-:*o*-:*m*-H, 3-Ph), 4.40 (2H, q, OCH_2), 0.70 (3H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 305.7 (W=C), 204.3 and 198.0 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 163.1 (O—CO), 142.6 (C3), 134.3 (*i*-C, 3-Ph), 134.1 (CH, 2-C), 129.6 (*i*-C, 3-benzoyloxy), 132.5, 130.6, 129.1 (1:2:2, *p*-:*o*-:*m*-CH, 3-benzoyloxy), 129.6, 128.5, 127.2 (2:1:2, *o*-:*p*-:*m*-CH, 3-Ph), 80.3 (OCH_2), 14.5 (CH_3). IR (hexane), cm^{-1} (%): 2067.1 (30), 1982.4 (5), 1944.9 (100) [ν(C≡O)]; (diffuse reflection) 1744.2 (30) [ν(OC=O)]. MS (70 eV), *m/e* (%), ^{184}W: 604 (10) [M$^+$], 576 (5), 548 (40), 520 (40), 492 (40), 464 (40) [M$^+$ − 5CO], 435 (30), 407 (30), 105 (100). Anal. Calcd for $C_{23}H_{16}O_8W$ (604.2): C, 45.72; H, 2.67. Found: C, 45.82; H, 2.83.

Pentacarbonyl[(2*Z*)-3-((*p*-(dimethylamino)benzoyl)-oxy)-1-ethoxy-3-phenyl-2-propenylidene]tungsten [(*Z*)-5c]. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1c**) (482 mg, 1.00 mmol) and 164 mg (1.00 mmol) of 4-(dimethylamino)benzoic acid (**4c**) in 3 mL of dichloromethane/diethyl ether (1:1) are treated as described above with 80 mg (0.80 mmol) of triethylamine at 20 °C. Chromatography after 5–6 h yields (*Z*)-**5c**, $R_f = 0.4$ in pentane/dichloromethane (1:

1) (480 mg, 74%, orange-red crystals from diethyl ether/pentane (1:1), mp 117 °C). ^{1}H NMR (C_6D_6): δ 8.15 and 6.25 (2:2, *o*-:*m*-H, 3-*p*-$Me_2NC_6H_4$), 8.00 (1H, s, 2-H), 7.65, 7.05, 6.85 (2:1:2, *o*-:*p*-:*m*-H, 3-Ph), 4.55 (2H, q, OCH_2), 2.30 (6H, NMe_2), 0.90 (3H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 306.0 (W=C), 204.3 and 198.0 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 162.0 (O—CO), 156.1 (C4', *p*-$Me_2NC_6H_4$), 143.0 (C3), 132.6 (*i*-C, 3-Ph), 132.4 (CH, C2), 119.6 (C1', 3-*p*-$Me_2NC_6H_4$), 132.4 and 111.4 (2:2, *o*-:*m*-CH, 3-*p*-$Me_2NC_6H_4$), 129.8, 128.5, 127.2 (2:1:2, *o*-:*p*-:*m*-CH; 3-Ph); 80.4 (OCH_2), 39.5 (CH_3, Me_2N), 14.6 (CH_3). IR (hexane), cm^{-1} (%): 2066.1 (30), 1980.2 (5), 1942.3 (100) [ν(C≡O)]; (diffuse reflection) 1727.6 (20) [ν(OC=O)]. MS (70 eV), *m/e* (%), ^{184}W: 649 (1) [M^+ + 2], 621 (2), 593 (4), 565 (4), 537 (2) [M^+ + 2 − 4CO], 508 (1) [M^+ + 1−5CO], 148 (100) [$Me_2NC_6H_4$-CO^+]. Anal. Calcd for $C_{25}H_{21}NO_8W$ (647.3): C, 46.39; H, 3.27; N, 2.16. Found: C, 47.29; H, 3.48; N, 2.38.

[(2*Z*)-3-Acetoxy-1-ethoxy-3-phenyl-2-propenylidene]-pentacarbonyltungsten [(*Z*)-5d]. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1c**) (482 mg, 1.00 mmol) and 60 mg (1.00 mmol) of acetic acid (**4d**) in 3 mL of dichloromethane/diethyl ether (1:1) are treated as described above with 80 mg (0.80 mmol) of triethylamine at 20 °C. Chromatography after 2−4 h yields (*Z*)-**5d**, R_f = 0.6 in pentane/diethyl ether (1:6) (395 mg, 73%, dark-brown crystals from diethyl ether/pentane (1:6), mp 99 °C). ^{1}H NMR (C_6D_6): δ 7.78 (1H, s, 2-H), 7.50, 6.95, 6.90 (2:1:2, *o*-:p-:*m*-H, 3-Ph), 4.50 (2H, q, OCH_2), 1.70 (3H, s, $COCH_3$), 1.00 (3H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 306.2 (W=C), 204.4 and 198.0 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 166.5 (O—CO), 142.6 (C3), 134.5 (*i*-C, 3-Ph), 132.4 (CH, 2-C), 131.2, 129.4, 127.1 (1:2:2, *p*-:*o*-:*m*-CH, 3-Ph), 80.2 (OCH_2), 20.5 ($COCH_3$), 14.9 (CH_3, Et). IR (hexane), cm^{-1} (%): 2067.3 (30), 1981.9 (5), 1944.5 (100) [ν(C≡O)]; (diffuse reflection) 1767.8 (20) [ν(OC=O)]. MS (70 eV), *m/e* (%), ^{184}W: 542 (10) [M^+], 486 (10), 458 (40), 430 (10), 402 (40) [M^+ − 5CO], 343 (40) [402 − $COCH_3$], 302 (50), 274 (40), 105 (100). Anal. Calcd for $C_{18}H_{14}O_8W$ (542.2): C, 39.88; H, 2.60. Found: C, 40.19; H, 2.89.

Pentacarbonyl[(2*Z*)-3-((α-cycloheptatrienyl)acetoxy)-1-ethoxy-3-phenyl-2-propenylidene]tungsten [(*Z*)-5e]. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1c**) (482 mg, 1.00 mmol) and 149 mg (1.00 mmol) of (α-cycloheptatrienyl)acetic acid (**4e**) in 3 mL of dichloromethane/diethyl ether (1:1) are treated as described above with 80 mg (0.80 mmol) of triethylamine at 20 °C. Chromatography after 8−10 h yields (*Z*)-**5e**, R_f = 0.4 in pentane/dichloromethane (3:1) (450 mg, 71%, dark brown crystals from diethyl ether/pentane (1:4), mp 71 °C). ^{1}H NMR (C_6D_6): δ 7.75 (1H, s, 2-H), 7.55, 6.98, 6.90 (2:1:2, *o*-:*p*-:*m*-H, 3-Ph), 6.45, 6.05, 5.05 (2:2:2H, each m, 2'-H bis 7'-H, cycloheptatrienyl), 4.60 (2H, q, OCH_2), 2.50 (2H, d, OC—CH_2), 2.30 (1H, m, 1'-H, cycloheptatrienyl), 1.03 (3H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 306.6 (W=C), 204.4 and 198.0 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 168.2 (O—CO), 142.2 (C3), 134.5 (*i*-C, 3-Ph), 132.6 (CH, C2), 131.2, 129.4, 126.0 (1:2:2, *p*-:*o*-:*m*-CH, 3-Ph), 131.5, 127.2, 124.6 (CH each, 2:2:2, cycloheptatrienyl), 80.2 (OCH_2), 37.8 (OC—CH_2), 35.7 (C1', cycloheptatrienyl), 15.1 (CH_3, Et). IR (hexane), cm^{-1} (%): 2067.3 (30), 1981.5 (5), 1943.8 (100) [ν(C≡O)]; (diffuse reflection) 1766.5 (20) [ν(OC=O)]. MS (70 eV), *m/e* ^{184}W: 632 (5) [M^+], 548 (10), 520 (10), 492 (10) [M^+ − 5CO], 443 (10), 304 (20), 105 (30), 91 (100) [$C_7H_7^+$]. Anal. Calcd for $C_{25}H_{20}O_8W$ (632.1): C, 47.46; H, 3.19. Found: C, 47.60; H, 3.37.

Pentacarbonyl[(2*Z*)-3-(((2-methyl-1-propenyl)carbonyl)oxy)-1-ethoxy-3-phenyl-2-propenylidene]tungsten[(*Z*)-5f]. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1c**) (482 mg, 1.00 mmol) and 100 mg (1.00 mmol) of 3,3-dimethylacrylic acid (**4f**) in 3 mL of dichloromethane/diethyl ether (1:1) are treated as described above with 80 mg (0.80 mmol) of triethylamine at 20 °C. Chromatography after 3 h yields (*Z*)-**5f**, R_f = 0.5 in pentane/dichloromethane (3:1) (436 mg, 75%, brown crystals from diethyl ether/pentane (1:6), mp 82 °C). ^{1}H NMR (C_6D_6): δ 7.85 (1H, s, 2-H), 7.65, 7.00, 6.90 (2:1:2, *o*-:*p*-:*m*-H, 3-Ph), 5.70 (1H, sept, ^4J = 1.1 Hz, 1'-H), 4.55 (2H, q, OCH_2), 2.00 and 1.45 (3H each, d each, ^4J = 1.1 Hz each, $=CMe_2$), 1.08 (3H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 306.1 (W=C), 204.4 and 198.1 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 162.3 and 161.7 (C_q each, O—CO and $=CMe_2$), 142.8 (C3), 134.8 (*i*-C, 3-Ph), 132.2 (CH, C2), 131.1, 129.4, 127.2 (1:2:2, *o*-:*p*-:*m*-CH, 3-Ph), 115.1 (OC—*C*H=), 80.1 (OCH_2), 27.3 and 20.5 [=C-(CH_3)$_2$], 14.6 (CH_3). IR (hexane), cm^{-1} (%): 2066.4 (30), 1979.2 (5), 1942.5 (100) [ν(C≡O)]; (diffuse reflection) 1744.3 (20) [ν(OC=O)]. MS (70 eV), *m/e* (%), ^{184}W: 582 (5) [M^+], 528 (5), 500 (4), 470 (10), 442 (5) [M^+ − 5CO], 441 (20), 413 (10), 385 (20), 357 (10), 329 (5), 301 (20), 215 (20), 187 (30), 168 (20), 149 (30), 105 (40), 83 (100) [OC—CH=CMe_2]. Anal. Calcd for $C_{21}H_{18}O_8W$ (582.2): C, 43.32; H, 3.12. Found: C, 43.42; H, 3.03.

Pentacarbonyl[(2*Z*)-3-(((1,2-diphenylethenyl)carbonyl)oxy)-1-ethoxy-3-phenyl-2-propenylidene]tungsten [(*Z*)-5g]. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1c**) (482 mg, 1.00 mmol) and 224 mg (1.00 mmol) of α-phenylcinnamic acid (**4g**) in 3 mL of dichloromethane/diethyl ether (1:1) are treated as described above with 80 mg (0.80 mmol) of triethylamine at 20 °C. Chromatography after 10 h yields (*Z*)-**5g**, R_f = 0.3 in pentane/dichloromethane (2:1) (520 mg, 74%, black crystals from diethyl ether/pentane (1:5) at −15 °C, mp 119 °C). ^{1}H NMR (C_6D_6): δ 8.10 (1H, s, 2'-H), 7.82 (1H, s, 2-H), 7.58, 7.26, 7.15, 6.95, 6.85 (2:2:3:5:3H, 3 Ph), 4.59 (2H, q, OCH_2), 1.10 (3H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): 306.4 (W=C), 204.4 and 198.0 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 164.0 (Cq, O—CO), 143.3 (CH, 2'-H), 142.7 (C3), 135.7, 134.7, 134.6 (*i*-C each, 3-Ph), 132.5 (CH, C2), 132.0 (Cq, C1'), 131.3, 130.4, 130.2, 129.5, 129.3, 128.9, 127.2 (2:4:1:2:1:2:1:2, CH each, 3-Ph), 80.3 (OCH_2), 15.2 (CH_3). IR (hexane), cm^{-1} (%): 2067.0 (30), 1981.6 (5), 1943.4 (100) [ν(C≡O)]; (diffuse reflection) 1733.5 (20) [ν(OC=O)]. MS (70 eV), *m/e* (%), ^{184}W: [M^+] missing, 622 (10) [M^+ − 3CO], 595 (10), 566 (10) [M^+ − 5CO], 471 (10), 304 (40), 302 (30), 294 (60), 207 (60), 179 (100) [Ph_2C=CH^+].

Decacarbonyl[(2*Z*)-μ-(((1,4-phenylene)dicarbonyl)dioxy)bis(1-ethoxy-3-phenyl-2-propen-3-yl-1-ylidene)]ditungsten [(*Z*)-5h]. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1c**) (482 mg, 1.00 mmol) and 83 mg (0.50 mmol) of terephthalic acid (**4h**) in 3 mL of dichloromethane/diethyl ether (1:1) are treated with 80 mg (0.80 mmol) of Et_3N as described above for 12 h, 20 °C. (*Z,Z*)-**5h**, R_f = 0.5 in pentane/diethyl ether (4:1) (420 mg, 74%, dark brown crystals from diethyl ether/pentane (1:1)). ^{1}H NMR (C_6D_6): δ 8.30 (4H, s, 3-*p*-C_6H_4), 7.80 (2H, s, 2 2-H), 7.65, 7.40, 7.30 (4:2:4, *o*-:*p*-:*m*-H, 2 3-Ph), 4.65 (2H, q, OCH_2), 1.15 (3H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 305.4 (W=C), 204.0 and 197.4 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 163.1 (O—CO), 141.2 (C3), 133.8 (*i*-C, 3-Ph), 133.6 (2 *i*-C, 3-*p*-C_6H_4), 132.7 (CH, C2), 131.5, 130.9, 129.5 (4:2:4, *o*-:*p*-:*m*-CH, 2 3-Ph); 127.0 (4 CH, 3-*p*-OOC—C_6H_4—COO), 80.0 (OCH_2), 14.9 (CH_3). IR (hexane), cm^{-1} (%): 2067.3 (20), 1982.4 (5), 1943.4 (100) [ν(C≡O)]; (diffuse reflection) 1743.6 (30) [ν(OC=O)]. MS (70 eV), *m/e* (%), ^{184}W: [M^+] missing. Anal. Calcd for $C_{40}H_{26}O_{16}W_2$ (1130.3): C, 42.50; H, 2.32. Found: C, 42.45; H, 2.38.

Pentacarbonyl{(2*E*)-3-[(4-carboxyphenyl)methylamino]-1-ethoxy-3-phenyl-2-propen-1-ylidene}tungsten [(*E*)-5i]. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1c**) (482 mg, 1.00 mmol) in 3 mL of dichloromethane/diethyl ether (1:1) in a 5-mL screw-top vessel is treated with 151 mg (1.00 mmol) of 4-(methylamino)benzoic acid (**4i**) to give red polar **5i**. The reaction is followed by TLC. After 1 day at 20 °C the solvent is replaced by diethyl ether. On dropwise addition of 2 mL of pentane a beige precipitate of (*E*)-**5i** is obtained (385 mg, 80%, red crystals from diethyl ether/pentane (1:1)). ^{1}H NMR (C_6D_6): δ 8.15 and 7.10 (2:2, 3-*p*-C_6H_4), 7.19 and 7.05 (3:2, 3-Ph), 7.80 (1H, s, 2-H), 4.15 (2H, q, OCH_2), 3.25 (NCH_3), 0.65 (3H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 270.0 (W=C), 224.3 and 218.0 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 170.7 (O—CO), 156.2 (C1', *p*-C_6H_4), 153.0 (C3), 132.8 (*i*-C, 3-Ph), 131.7 (CH, C2), 125.3 (C4', 3-*p*-C_6H_4), 129.1 and 126.8 (2:2,

3-*p*-C_6H_4), 130.0, 128.5, 127.6 (2:1:2, *o*-:*p*-:*m*-CH, 3-Ph), 77.4 (OCH_2), 42.5 (NCH_3), 14.0 (CH_3, Et). IR (hexane), cm^{-1} (%): 2058.5 (30), 1989.1 (5), 1926.1 (100) [ν(C≡O)]; (diffuse reflection) 3455 (5) [ν(NH)], 1681.5 (30) [ν(OC=O)]. MS (70 eV), *m/e* (%), ^{184}W: [M^+] missing. Anal. Calcd for $C_{24}H_{19}NO_8W$ (633.3): C, 45.52; H, 3.02; N, 2.21. Found: C, 45.73; H, 3.45; N, 2.32.

Decarbonylditungsten Bis(carbene) Complex (*E,Z*)-5k. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1c**) (1060 mg, 2.20 mmol) and 151 mg (1.00 mmol) of 4-(methylamino)benzoic acid (**4i**) in 3 mL of dichloromethane/diethyl ether (1:1) are reacted for 24 h at 20 °C and then treated with 80 mg (0.80 mmol) of Et_3N. Isolation by chromatography after 24 h at 20 °C as above yields (*E,Z*)-**5k**, R_f = 0.5 in pentane/diethyl ether (3:1) (835 mg, 75% dark brown crystals from diethyl ether/pentane (1:1), mp 147 °C). ^1H NMR (C_6D_6): δ 7.95 (1H, s, =CH, 2-H, carboxyl), 8.15 and 6.65 (2:2, 3-*p*-C_6H_4), 7.55, 7.05, 6.98 (2:1:2, 3-Ph carboxyl), 6.95 and 6.85 (3:2, m each broad, 3-Ph, amino), 7.92 (1H, s, 2-H, amino), 4.50 (2H, q, OCH_2), 4.20 (2H, q, NCH_2), 2.70 (NCH_3), 0.95 (3H, t, OCH_2CH_3), 0.50 (3H, t, NCH_2CH_3). ^{13}C NMR (C_6D_6): δ 306.0 and 284.5 (W=C each), 204.2 and 199.8 as well as 204.1 and 197.3 [1:4 each, *trans*- and *cis*-CO, $W(CO)_5$], 162.1 (O—CO), 154.9 (*i*-C, *p*-C_6H_4), 150.4 and 142.1 (C_q each, C3), 137.5 and 134.2 (C_q each, *i*-C, 3-Ph), 132.5 and 127.3 (CH each, C2), 131.8, 131.3, 129.6, 128.9, 127.0 (CH each, 1:2:2:4:4:1, 2 Ph and 3-*p*-C_6H_4), 127.6 (*i*-C, 3-*p*-C_6H_4), 80.2 and 77.3 (OCH_2 each), 41.6 (NCH_3), 14.8 and 14.6 (CH_3 each, Et). IR (hexane), cm^{-1} (%): 2064.7 (20), 1982.4 (5), 1936.2 (100) [ν(C≡O)]; (diffuse reflection) 1743.9 (30) [ν(OC=O)]. MS (70 eV), *m/e* (%), ^{184}W: [M^+] missing. Anal. Calcd for $C_{40}H_{29}NO_{14}W_2$ (1115.4): C, 45.52; H, 2.62; N, 1.26. Found: C, 45.45; H, 2.98; N, 1.00.

Pentacarbonyl[1-cyclohexyl-3-ethoxy-2,5-dihydro-5-methoxy-5-phenyl)-2*H*-pyrrol-2-ylidene]chromium (9b). Cyclohexyl isocyanide (**8a**) (119 mg, 1.10 mmol) is added to a suspension of 382 mg (1.00 mmol) of (orange) pentacarbonyl-[1-ethoxy-3-methoxy-3-phenylpropenylidene]chromium[9] [(*E*)-**7b**] in 3 mL of pentane and stirred for 2 days at 20 °C in an airtight 5-mL screw-top vessel. **9b** is obtained in yellow crystals, 417 mg, 85%, R_f = 0.2 in dichloromethane. ^1H NMR (C_6D_6, +20 °C): δ 7.90 and 6.90 (1H each, s each broad, *o*-H, Ph), 7.15 (3H, s broad, *m*- and *p*-H, Ph), 5.25 (1H, t, CHN), 4.70 (1H, s, 4-H), 3.30 (2H, q broad, OCH_2, Et), 3.00 (3H, s, 5-OCH_3), 2.10, 1.80, 1.35, 0.95 (3:1:4:2H, m each, cyclohexyl), 1.30 (3H, t, CH_3, Et). ^{13}C NMR ($CDCl_3$): δ 265.2 (Cr=C), 225.0 and 218.8 [1:4, *cis*- and *trans*-CO $Cr(CO)_5$], 160.2 (Cq, C3), 137.0 (C_q, *i*-C, 5-Ph), 132.1 and 127.8 (CH each, dynamically broadened each, *o*-C each, Ph), 129.1, and 126.3 (CH each, 2:1, *m*- and *p*-C, Ph), 108.3 (C_q, C5), 105.9 (CH, C4), 68.5 (CHN), 66.7 (OCH_2), 52.4 (OCH_3), 33.3, 31.8, 26.6, 26.4, 25.6 (CH_2 each, cyclohexyl), 14.0 (CH_3, Et). IR (hexane), cm^{-1} (%): 2055.2 (30), 1977.8 (5), 1933.4 (100) [ν(C≡O)]. MS (70 eV), *m/e* (%): 491 (50) [M^+], 463 (25), 425 (30), 407 (20), 379 (60), 351 (60) [M^+ − 5CO], 336 (80), 322 (40), 55 (100). Anal. Calcd for $C_{24}H_{25}CrNO_7$ (491.5): C, 58.65; H, 5.13; N, 2.85. Found: C, 58.84; H, 5.40; N, 3.07.

4-(Benzoyloxy)-*N*-*tert*-butyl-2-ethoxy-4-phenyl-1,3-butadien-1-imine [(*Z*)-11b] and 4-(Benzoyloxy)-*N*-*tert*-butyl-2-ethoxy-1-oxo-4-phenyl-3-butenamide [(*Z*)-14b]. *tert*-Butyl isocyanide (**8b**) (17 mg, 0.20 mmol) is added to 47 mg (0.10 mmol) of [(2*Z*)-3-(benzoyloxy)-1-ethoxy-3-phenyl-2-propenylidene]pentacarbonylchromium [(*Z*)-**5a**] or 65 mg (0.10 mmol) of [(2*Z*)-3-(benzoyloxy)-1-ethoxy-3-phenyl-2-propenylidene]pentacarbonyltungsten [(*Z*)-**5b**] and hexamethylbenzene as an internal standard in 1 mL of C_6D_6 at 20 °C. The reaction mixture turns yellow within a few minutes with generation of (*Z*)-**11b** and **12b** (as well as **12a**). Integration of the ^1H NMR signals indicates an essentially quantitative reaction. Chromatography on silica leads to hydrolysis of (*Z*)-**11b** and formation of colorless (*Z*)-**14b**.

(*Z*)-**11b**: ^1H NMR (C_6D_6) δ 8.20, 7.15, 7.05 (2:1:2, benzoyloxy), 7.35, 6.95, 6.80 (2:1:2H, 3-Ph), 6.30 (1H, s, 3-H), 3.50 (2H, q, OCH_2), 1.10 (9H, s, CH_3, *t*-Bu), 0.95 (3H, q, CH_2CH_3); ^{13}C NMR (C_6D_6) δ {199.4 and 195.1 [1:4, $W(CO)_5$ of **12a**], 155.8 [CNR of **12a**]}, 197.4 (NCC), 164.1 (OC=O), 142.4 (C_q, C4), 163.3 (*i*-C, 4-Ph), 133.5, 130.8, 128.8 (CH each, 1:2:2 benzoyloxy, 128.9, 127.9, 124.4 (CH each, 1:2:2, Ph), 112.7 (C_q, C2), 110.6 (CH, C3), 67.0 (OCH_2), 61.6 (C_q, *t*-Bu), {57.9 [CMe_3 of **12a**], 30.5 [$C(CH_3)_3$ of **12**]}, 29.9 (3 CH_3, *t*-Bu), 15.2 (CH_2CH_3); IR (diffuse reflection) [cm^{-1} (%)] (**12a**) 2162.4 (30) [ν(C≡C)], 2067.4 (30) and 1937.2 (100) [ν(C≡O)]; IR (diffuse reflection) [cm^{-1} (%)] (**11b**) 1994.4 (25) [ν(N=C=C)], 1739.8 [ν(C=O)]; MS (70 eV) [*m/e* (%)] 363 (20) [M^+], 307 (40) [$M^+ - C_4H_8$], 264 (10), 251 (10), 202 (30), 174 (20), 105 (100). Anal. Calcd for $C_{23}H_{25}NO_3$ (363.2): C, 76.01; H, 6.93; N, 3.85. Found: C, 75.98; H, 6.92; N, 3.95.

(*Z*)-**14b**: ^1H NMR (C_6D_6) δ 8.30, 7.40, 7.15, 7.10, 6.95 (2:2:1:2:3H, 2 Ph), 6.50 (1H, s br, NH), 5.95 and 4.70 (1H each, AB system, ^3J = 8.3 Hz, 2-H and 3-H), 3.55 and 3.35 (1H each, diastereotope OCH_2), 1.25 (9H, s, *t*-Bu), 1.00 (3H, t, CH_3, Et); MS (70 eV) [*m/e* (%)] 381 [M^+], 325 (20) [$M^+ - C_4H_8$], 282 (30) [M^+ − *t*-BuNHCO], 281 (30), 105 (100) [$PhCO^+$]. Anal. Calcd for $C_{23}H_{27}NO_4$ (381.5): C, 72.41; H, 7.13; N, 3.67. Found: C, 72.52; H, 7.22; N, 3.54.

***N*-*tert*-Butyl-4-((4-(dimethylamino)benzoyl)oxy)-2-ethoxy-4-phenyl-1,3-butadien-1-imine [(*Z*)-11c].** *tert*-Butyl isocyanide (**8b**) (17 mg, 0.20 mmol) is added to 52 mg (0.10 mmol) of pentacarbonyl[(2*Z*)-3-((4-(dimethylamino)benzoyl)-oxy)-1-ethoxy-3-phenyl-2-propenylidene]tungsten [(*Z*)-**5c**] and hexamethylbenzene as an internal standard in 1 mL of C_6D_6 at 20 °C. The reaction mixture turns yellow within a few minutes with generation of (*Z*)-**11c** and **12a**. Integration of the ^1H NMR signals indicates an essential quantitative reaction. Chromatography on silica leads to hydrolysis of (*Z*)-**11c**. ^1H NMR (C_6D_6): δ 8.30 and 6.30 (2:2H, *p*-C_6H_4), 7.30, 7.05, 6.90 (2:2:1, 3-Ph), 6.30 (1H, s, 3-H), 3.50 (2H, q, OCH_2), 2.30 (6H, s, Me_2N), 1.10 (9H, s, CH_3, *t*-Bu), 1.05 (3H, q, CH_2CH_3). ^{13}C NMR (C_6D_6): δ {199.4 and 195.1 [1:4, $W(CO)_5$ of **12a**], 153.9 [CNR of **12a**]}, 197.0 (NCC), 164.4 (OC=O), 153.9 (C_q, C-NMe_2), 142.9 (C_q, C4), 136.9 (*i*-C, 4-Ph), 128.9, 127.9, 124.6 (CH each, 1:2:2, 4-Ph), 126.8, 111.3 (CH each, 2:2, *p*-C_6H_4), 117.6 (C_q, *i*-C, *p*-C_6H_4), 112.8 (C_q, C2), 110.9 (CH, C3), 67.1 (OCH_2), 61.5 (C_q, *t*-Bu) {57.9 [CMe_3 of **12a**], 30.5 [$C(CH_3)_3$ of **12a**]}, 39.6 (CH_3, NMe_2), 30.8 (3 CH_3, *t*-Bu), 15.9 (CH_2CH_3). IR (diffuse reflection), cm^{-1} (%): **12a** 2162.4 (30) [ν(C≡C)], 2067.4 (30) and 1937.2 (100) [ν(C≡O)]; **11c** 1985.5 (25) [ν(N=C=C)], 1719.3 [ν(C=O)].

4-Acetoxy-*N*-*tert*-butyl-2-ethoxy-4-phenyl-1,3-butadien-1-imine [(*Z*)-11d]. *tert*-Butyl isocyanide (**8b**) (17 mg, 0.20 mmol) is added to 54 mg (0.10 mmol) of [(2*Z*)-3-acetoxy-1-ethoxy-3-phenyl-2-propenylidene]pentacarbonylchromium [(*Z*)-**5d**] and hexamethylbenzene as an internal standard in 1 mL of C_6D_6 at 20 °C. The reaction mixture turns yellow within a few minutes with generation of (*Z*)-**11d** and **12a**. Integration of the ^1H NMR signals indicates an essentially quantitative reaction. Chromatography on silica leads to hydrolysis of (*Z*)-**11d**. ^1H NMR (C_6D_6): δ 7.30, 7.05, 6.90 (2:2:1, 3-Ph), 6.20 (1H, s, 3-H), 3.50 (2H, q, OCH_2), 2.00 (CH_3, Ac), 1.10 (9H, s, CH_3, *t*-Bu), 1.00 (3H, q, CH_2CH_3). ^{13}C NMR (C_6D_6): δ 94.2 (NCC), 167.9 (OC=O), 142.4 (C_q, C4), 137.3 (*i*-C, 4-Ph), 128.9, 127.9, 124.4 (CH each, 1:2:2, Ph), 112.3 (C_q, C2), 110.4 (CH, C3), 67.0 (OCH_2), 61.5 (C_q, *t*-Bu), 30.3 (3 CH_3, *t*-Bu), 20.6 (CH_3, Ac), 15.5 (CH_2CH_3). IR (diffuse reflection), cm^{-1} (%): **12a** 2162.4 (30) [ν(C≡C)], 2067.4 (30) and 1937.2 (100) [ν(C≡O)]; **11d** 1987.8 (25) [ν(N=C=C)], 1764.3 [ν(C=O)]. MS (70 eV), *m/e* (%): 301 (15) [M^+], 412 (100) [$M^+ - C_4H_8$]. Anal. Calcd for $C_{18}H_{23}NO_3$ (301.4): C, 71.73; H, 7.69; N, 4.65. Found: C, 71.98; H, 7.45; N, 4.87.

***N*-*tert*-Butyl-4-((α-cycloheptatrienyl)acetoxy)-2-ethoxy-4-phenyl-1,3-butadien-1-imine [(*Z*)-11e].** *tert*-Butyl isocyanide (**8b**) (17 mg, 0.20 mmol) is added to 63 mg (0.10 mmol) of pentacarbonyl[(2*Z*)-3-((α-cycloheptatrienyl)acetoxy)-1-ethoxy-

3-phenyl-2-propenylidene]chromium [(*Z*)-**5e**] and hexamethylbenzene as an internal standard in 1 mL of C_6D_6 at 20 °C. The reaction mixture turns yellow within a few minutes with generation of (*Z*)-**11e** and **12a**. Integration of the ^{1}H NMR signals indicates an essential quantitative reaction. ^{1}H NMR (C_6D_6): δ 7.32, 7.10, 7.05 (2:2:1, 3-Ph), 6.48, 6.06, 5.20 (2:2:2H, each m, cycloheptatrienyl), 6.17 (1H, s, 3-H), 3.48 (2H, q, OCH_2), 2.85 (2H, d, $OC-CH_2$), 2.40 (1H, m, 1′-H), 1.20 (9H, s, CH_3, *t*-Bu), 1.05 (3H, q, CH_2CH_3) {0.80 [9H, *t*-Bu of **12a**]}. ^{13}C NMR (C_6D_6): δ {199.2 and 196.4 [1:4, $W(CO)_5$ of **12a**], 153.9 [CNR of **12a**]}, 198.4 (NCC), 170.7 (OC=O), 143.9 (C_q, C4), 131.4, 128.9, 124.6 (CH each, 2:2:2, cycloheptatrienyl), 127.9, 125.7, 125.3 (1:2:2; *p*-:*o*-:*m*-CH; 3-Ph), 113.6 (C_q, C2), 111.8 (CH, C3), 68.4 (OCH_2), 63.0 (C_q, *t*-Bu) {59.1 [CMe_3 of **12a**], 30.5 [$C(CH_3)_3$ of **12a**]}, 39.2 ($OC-CH_2$), 37.2 (CH, C1′, cycloheptatrienyl), 31.7 (3 CH_3, *t*-Bu), 15.8 (CH_2CH_3). IR (diffuse reflection), cm^{-1} (%): **12a** 2162.4 (30) [ν(C≡C)], 2067.4 (30) and 1937.2 (100) [ν(C≡O)]; **11e** 1986.4 (25) [ν(N=C=C)], 1759.1 [ν(CO)].

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Supplementary Material Available: Tables of crystal data and details of the structure solution, positional and displacement parameters, bond distances and angles, and thermal parameters and a figure showing the structure of the compound (7 pages). Ordering information is given on any current masthead page.

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