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Organic Syntheses via Transition Metal Complexes. 73.[1] Acylation of Methylcarbene Complexes (M = Cr, W) with Formation of [2-(Acyloxy)ethenyl]-, [4-(Acyloxy)butadienyl]-, and Alkynylcarbene Complexes

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[2-(Acyloxy)ethenyl]carbene complexes $(CO)_5M{=}C(OEt){-}CH{=}C(OCOR)R$ [(*Z*)-**4**] (R = *t*-Bu, *i*-Pr, *c*-Pr, Ph, *p*-tolyl, *p*-anisyl) are obtained by acylation of methylcarbene complexes $(CO)_5M{=}C(OEt)CH_3$ (**1**) (M = Cr, W) with carboxylic acid chlorides R−COCl (**2**) (R = *t*-Bu, *i*-Pr, *c*-Pr, Ph, *p*-tolyl, *p*-anisyl, *o*-C_6H_4COCl) in the presence of Et_3N in 53−78% isolated yields. Side reactions include the formation of nonconjugated alkenylcarbene complexes $(CO)_5M{=}C(OEt){-}CH_2{-}C(OCO\textit{i}Pr){=}CMe_2$ (**5b,h**) (R = *i*-Pr) and of alkynylcarbene complexes $(CO)_5M{=}C(OEt){-}C{\equiv}CR$ (**6a,g,i**) (R = *t*-Bu, *c*-Pr). The tungsten complexes (*Z*)-**4d−f** (R = aryl) undergo a metathesis to give (4-(acyloxy)butadienyl)carbene complexes $(CO)_5W{=}C(OEt){-}CH{=}C(OEt){-}CH{=}C(OCOR)R$ [(*E,Z*)-**7d−f**]. (*E,Z*)-**7f** (R = *p*-anisyl) was characterized by X-ray diffraction. It crystallizes in space group $P\bar{1}$ with cell parameters $a = 9.696(2)$ Å, $b = 11.751(2)$ Å, $c = 13.909(3)$ Å, $\alpha = 100.79(2)°$, $\beta = 93.06(2)°$, $\gamma = 102.90(1)°$, $Z = 2$, $R_1 = 0.0345$, and $wR_2 = 0.0770$.

[2-(Acyloxy)ethenyl]carbene Complexes (*Z*)-4

Protons attached to the α-carbon atom of methylcarbene complexes $(CO)_5M{=}C(OEt)CH_3$ (**1**) [M = Cr (**a**), W (**b**)] undergo a rapid base-catalyzed hydrogen/deuterium exchange[2] and are easily replaced also by many other electrophiles.[3] Recent studies include base-catalyzed condensations with acid amides[4,5] $O{=}C(NR_2)R'$ to give (2-aminoethenyl)carbene complexes $(CO)_5M{=}C(OEt){-}CH{=}C(NR_2)R'$, as well as substitution reactions with cationic olefin complexes,[6,7] tropylium ions,[8] and complexed cyclohexadienyl- or cycloheptadienyl cations,[9] which yield α-mono- as well as α-disubstituted methylcarbene complexes. Casey *et al.* have found that the acetylation of alkylcarbene complexes (M = Cr, W) initially leads to α-monoacetylated products, which can be obtained in good yields in the absence of enolizable protons,[3b] but otherwise undergo an O-acetylation to give *E*/*Z* mixtures of enol acetates.[3a]

We report on an efficient one-pot procedure for the acylation of **1** by a variety of acyl chlorides **2** in the presence of triethylamine. This reaction is catalyzed by *p*-(dimethylamino)pyridine (DMAP)[10] and leads to the formation of dark-brown stable enol esters **4** in 53−78% isolated yields (Scheme 1). Thus in principle the reaction of **1** with **2** follows a pattern well-known for the acylation of enolizable aldehydes or ketones. While these compounds usually yield mixtures of regioisomers resulting from C- and O-alkylation, of which the latter also form (*E*) and (*Z*) stereoisomers,[11] the acylation of **1** is regiospecific and gives enol esters **4** with the (*Z*) configuration only, except for R = *i*-Pr and *c*-Pr (Scheme 1). The reaction thus provides further and efficient access to compounds **4**, which are obtained otherwise by the addition of carboxylic acid to alkynylcarbene complexes.[1] The acylation of **1** can be extended to

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[1] Part 72: Aumann, R.; Jasper, B.; Läge, M.; Krebs, B. *Organometallics*, preceding article in this issue.

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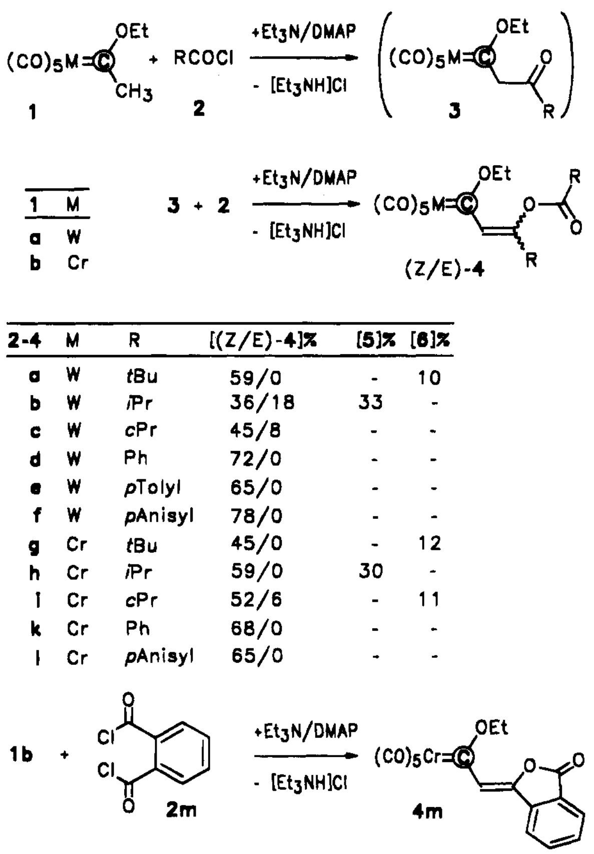
Scheme 1. [2-(Acyloxy)ethenyl]carbene Complexes (*Z*)-4 by Acylation of Methylcarbene Complexes 1 (M = Cr, W)



2-4	M	R	[(Z/E)-4]%	[5]%	[6]%
a	W	*t*Bu	59/0	-	10
b	W	*i*Pr	36/18	33	-
c	W	*c*Pr	45/8	-	-
d	W	Ph	72/0	-	-
e	W	*p*Tolyl	65/0	-	-
f	W	*p*Anisyl	78/0	-	-
g	Cr	*t*Bu	45/0	-	12
h	Cr	*i*Pr	59/0	30	-
i	Cr	*c*Pr	52/6	-	11
k	Cr	Ph	68/0	-	-
l	Cr	*p*Anisyl	65/0	-	-

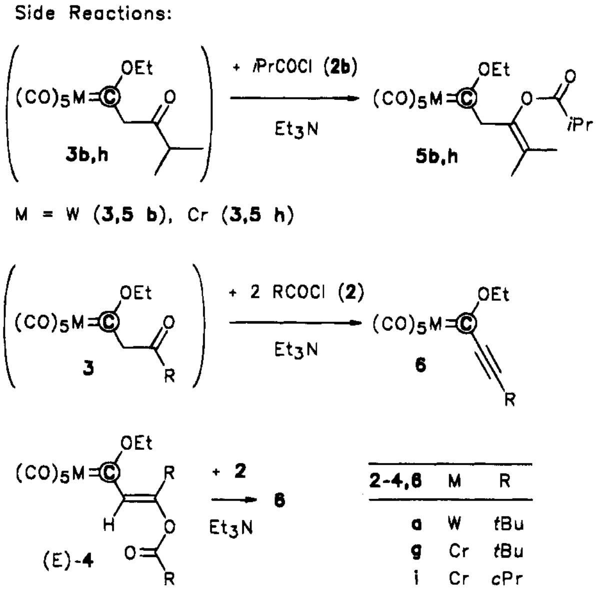
dicarboxylic acid dichlorides, e.g. **2m**, and in this case leads to the formation of γ-lactones **4m** (Scheme 1).

A salient feature in the preparation of **1** is the marked influence of the reaction conditions as well as the substituents (see below) on the reaction course. Monoacyl derivatives **3**, which are generated as intermediates usually undergo a fast (charge controlled) O-acylation to **4**. This is due to the fact that the methylene group of **3** is activated by a metal–carbene as well as by an acyl moiety and for this reason is even more reactive toward a base-catalyzed acylation than is **1**.

Spectroscopy

4 exhibits characteristic NMR chemical shifts for the hydrogen atoms 2-H (δ 6.90–8.10 ppm) and OCH_2 (δ 4.40–4.70 ppm) as well as for the carbon atoms C1 (M = Cr, δ 329–334 ppm; M = W, δ 303–309 ppm), C2 (δ 127–136 ppm), and C3 (δ 141–156 ppm). Significant deviations are observed between δ(C1) of tungsten **6a–f** and chromium complexes **6g–l** (see also literature[1]). The tungsten complexes (*E*)-**4b,c** (R = *i*-Pr, *c*-Pr) and the corresponding chromium complexes (*E*)-**4i** (R = *c*-Pr), which are minor reaction products, can be distinguished from the (*Z*) isomers by the low-field shifts of C2 and C3 (due to a γ-effect) and of 2-H and 1′-H (due to the deshielding effect of the C=O group) in the NMR spectra and by the bathochromic shift of the [ν(C=C)] bands of about 10 cm^{-1} in the IR spectra. The configurations of **4a–l** have been assigned by NOE measurements, which indicate an interaction between 2-H and R. The structural assignments are also based on a X-ray analysis of a prototype.[1]

Scheme 2. Minor Products Obtained on Acylation of 1



2-4,6	M	R
a	W	*t*Bu
g	Cr	*t*Bu
i	Cr	*c*Pr

Alkynylcarbene Complexes

The acylation of **1** with aliphatic acyl chlorides **2a–c** yields in addition to **4** also small amounts of nonconjugated alkenylcarbene complexes **5b,h** (R = *i*-Pr) as well as alkynylcarbene complexes **6a,g,i** (R = *t*-Bu, *c*-Pr) (Schemes 1 and 2). Compounds **5** can be derived from reactions of **1** with enolizable aliphatic acyl chlorides only (e.g. **2b**, R = *i*-Pr) and may result from kinetically controlled enolization of the monoacyl intermediates **3** (e.g. **3b,h**).

Alkynylcarbene complexes **6a,g,i** are formed on acylation of **1**, if an excess of *3* equiv of nonenolizable acyl chlorides **2a,c** is applied. (*Z*)-**4a,g** could easily be excluded as precursors to **6a,g** by control experiments. It is quite obvious that the latter compounds were generated much faster from **1** (1–2 h) than they were obtained by acylation of (*Z*)-**4a,g** (3–4 days) under otherwise identical reaction conditions. (*E*)-**4a,g** appears to be a plausible candidate for an acyl-induced *syn* elimination to give **6a,g** and for this reason may not be accumulated and detected in the reaction mixture of **1a,b** with **2a** (Scheme 2).

1-Metalla 1,3,5-Trienes from 1-Metalla 1,3-Dienes

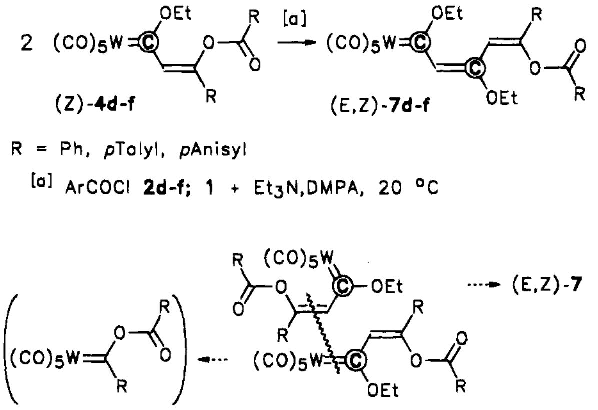
The acylation of **1** affords enol esters **4** in good yields, only if proper reaction conditions are applied. The tungsten aryl complexes (*Z*)-**4d–f** prove to be stable for a few hours in the reaction medium in which they are generated and afterward begin to transform into butadienylcarbene complexes (*E,Z*)-**7d–f** (Scheme 3). The reaction can be followed by TLC and is completed within 0.5–1.5 days at 20 °C, after which time (*Z,E*)-**7** may be isolated in 40–45% yields as the only detectable organometallic products except for $W(CO)_6$. The structural feature most characteristic of **7** is the presence of an enol ester *and* an enol ether unit in the carbon chain of the carbene ligand.

The remarkable chain extension of **4** by two carbon atoms is observed on acylation of the *tungsten* complex **1a**, but not so with the chromium complex **1b**. Stable

Table 1. Selected ^{13}C (^{1}H) NMR Shifts (C_6D_6, δ Values, [ν(COO)] Vibrations (cm^{-1}) in the IR Spectra, and Yields of the 1-Metalla 1,3,5-Trienes (*Z,E*)-7d-f

(*Z,E*)-7	C1	C2	C3	C4	C5	1-OCH_2	3-OCH_2	COO	2-*H*	4-H	1-OCH_2 (H)	3-OCH_2 (H)	ν(COO)	ν(C=C)	[7], %
d	294.5	133.9	156.4	112.1	154.4	79.3	65.4	163.6	7.08	7.05	4.50	3.50	1743.1	1623.3, 1511.0	40
e	293.8	130.8	157.0	111.3	155.1	79.2	65.4	163.7	7.20	7.05	4.50	3.50	1742.8	1620.1, 1516.5	42
f	293.0	132.8	157.4	110.2	155.3	79.2	65.4	163.3	7.10	7.05	4.52	3.52	1738.6	1574.6, 1514.6	45

Scheme 3. Butadienylcarbene Complexes (*E,Z*)-7d–f Derived from (*Z*)-4d–f



1-tungsta 1,3,5-trienes **7** are obtained with aroyl chlorides **2d**–f, but not with alkanoyl chlorides. Though mechanistic studies on the transformation of 1-metalla 1,3-dienes **4** into 1-metalla 1,3,5-trienes **7** have not been carried out yet, some experimental details point to a reaction path suggested in Scheme 3. Because production of **7** is observed after **1** has been consumed completely, **4** remains the only organometallic source of **7**. A metathesis of **4** would produce **7** and a 1-acylcarbene complex, which is expected to decompose rapidly and yield $W(CO)_6$. Because the thermolysis of **4** under inert conditions does not lead to the formation **7**, nor does its reaction with triethylamine or an aroyl chloride alone, we suggest that the metathesis of **4** may be catalyzed by a tungsten species, which is generated as a side product during the reaction of **1** with **2**.

The structural assignment of **7** is based on ^{13}C NMR spectra, which indicate the presence of *one* carbene carbon atom and of two OCH_2 groups. Of the latter only one exhibits the strong downfield shifts in the ^{13}C and ^{1}H NMR spectra, which are expected for a 1-ethoxycarbene unit (Table 1). The configuration of (*E,Z*)-**7d–f** is uniform and was determined by NOE measurements, but a crystal structure analysis of (*E,Z*)-**7f** was necessary to unravel more structural details.

Crystal Structure Analysis of (*E,Z*)-7f

Figure 1 shows the molecular structure, and Tables 2 and 3 give the data for the X-ray structure analysis of (*E,Z*)-**7f**. The compound forms triclinic crystals in the space group P$\bar{1}$. The coordination plane of the carbene carbon atom approximately bisects the angle between two cisoid CO groups at the tungsten atom (C1–W1–C6–O6 −49.4°). The conjugated diene portion shows an alternating CC double-bond, single-bond, double-bond sequence [1.374(6) Å (C9–C10), 1.443(7) Å (C10–C13), 1.345(6) Å (C13–C14)]. The C9–C10 distance is somewhat elongated as compared to typical bond distances found in many organic conjugated diene systems (see e.g.: 1,3-butadiene, 1.330 Å (C1–C2), 1.455 Å (C2–C3)] due to the delocalization of the ethoxy group into the adjacent C=C bond. The bond lengths C14–O8 1.391(5) Å and C15–O8 1.372(6) Å are in the range expected for single bonds between sp^2 hybridized carbon and sp^2 hybridized oxygen atoms. The carboxylic group is strongly distorted against the C13–C14 bond (C13–C14–O8–C15 −73.4°). There seems to be little delocalization of the lone pairs at O8 into the adjacent C=C bond, as is also observed with compounds of type **4**.[1] Thus the distance O8–C14 1.391(5) Å is much longer than O7–C10 1.351(5) Å and O6–C6 1.339(5) Å. The W=C–C=C–C=C unit exhibits a bent sickle shape with significant deviations from planarity (C9–C10–C13–C14 173.8° and W1–C6–C9–C10 −162.3°). These are much smaller than is observed with the 1-aminocarbene complex $(CO)_5W=C(NEt_2)-C(Me)=C(OEt)-CH=CH(Ph)$ (W=C–C=C −92°).[12]

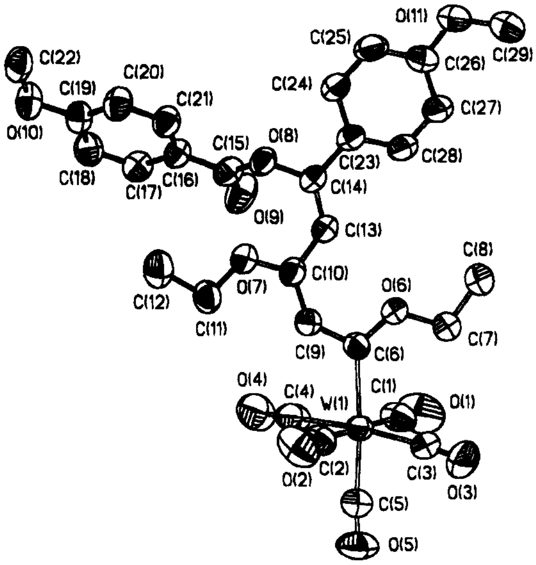


Figure 1. Molecular structure of (*E,Z*)-**7f** with selected bond lengths (Å) and angles (deg): W(1)–C(6) 2.210(5), W(1)–C(5) 2.015(6), W(1)–C(1) 2.023(6), C(6)–C(9) 1.438(6), C(9)–C(10) 1.374(6), C(10)–C(13) 1.443(7), C(13)–C(14) 1.345(6), O(6)–C(6), 1.339(5), O(7)–C(10) 1.351(5), O(8)–C(14) 1.391(5), O(8)–C(15) 1.372(6), O(9)–C(15) 1.197(6); C(5)–W(1)–C(6) 175.8(2), C(1)–W(1)–C(6) 92.8(2), O(6)–C(6)–W(1) 129.5(3), O(6)–C(6)–C(9) 111.0(4), C(10)–C(9)–C(6) 131.9(4), C(9)–C(10)–C(13) 125.2(4), C(14)–C(13)–C(10) 130.0(4).

Experimental Section

All operations were performed under argon. Solvents were dried by distillation from sodium/benzophenone. Melting points are uncorrected. Instrumentation: ^{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.

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Table 2. Crystal Data and Structure Refinement for (*E,Z*)-7f

empirical formula	$C_{29}H_{26}O_{11}W$
fw	734.35
temp, K	293(2)
wavelength, Å	0.710 73
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	
a, Å	9.696(2)
b, Å	11.751(2)
c, Å	13.909(3)
α, deg	100.79(2)
β, deg	93.06(2)
γ, deg	102.90(1)
vol, Å^3	1509.9
Z	2
density (calcd), Mg/m^3	1.615
abs coeff, mm^{-1}	3.882
F(000)	724
cryst size, mm	0.22 × 0.15 × 0.05
θ range for data collcn, deg	3.0−29.3
index ranges	$0 \le h \le 12$, $-15 \le k \le 14$, $-17 \le l \le 17$
no. of reflns collcd	6562
no. of ind reflns	6174 [*R*(int) = 0.0151]
refinement method	full-matrix least squares on F^2
data/restraints/params	6173/0/370
goodness-of-fit on F^2	1.094
final *R* indices [$i > 2\sigma(I)$]	$R_1 = 0.0345$, $wR_2 = 0.0770$
R indices (all data)	$R_1 = 0.0425$, $wR_2 = 0.0801$
largest diff peak and hole, e Å^{-3}	+0.941 and −0.613

[a] Further details of the crystal structure (complete bond lengths 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-57915, the name of the authors, and the journal citation.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for (*E,Z*)-7f[a]

	x	*y*	*z*	*U*(eq)
W(1)	2125(1)	2820(1)	4273(1)	50(1)
O(1)	2742(7)	5637(4)	4647(5)	124(2)
O(2)	1549(6)	1(4)	3691(5)	108(2)
O(3)	−487(5)	2782(5)	5550(4)	106(2)
O(4)	5012(5)	2980(6)	3278(4)	114(2)
O(5)	3821(6)	3204(5)	6358(3)	109(2)
O(6)	20(4)	3027(3)	2467(2)	65(1)
O(7)	1882(4)	975(3)	339(3)	68(1)
O(8)	974(3)	1775(3)	−1183(2)	57(1)
O(9)	3088(4)	3062(4)	−678(3)	84(1)
O(10)	4778(4)	−647(3)	−4052(3)	73(1)
O(11)	−3390(4)	4729(4)	−2158(3)	78(1)
C(1)	2493(7)	4616(5)	4482(5)	75(2)
C(2)	1767(6)	1013(5)	4072(4)	66(1)
C(3)	407(6)	2775(5)	5043(4)	68(1)
C(4)	3971(6)	2916(6)	3626(4)	73(2)
C(5)	3223(6)	3033(5)	5592(4)	72(1)
C(6)	1057(5)	2557(4)	2777(3)	51(1)
C(7)	−615(7)	3789(6)	3159(4)	82(2)
C(8)	−1700(7)	4191(7)	2590(5)	90(2)
C(9)	1510(5)	1817(4)	1970(3)	55(1)
C(10)	1304(5)	1716(4)	969(4)	56(1)
C(11)	2670(6)	208(5)	701(4)	67(1)
C(12)	3043(7)	−576(5)	−188(5)	84(2)
C(13)	492(5)	2371(4)	481(3)	57(1)
C(14)	321(5)	2416(4)	−476(3)	53(1)
C(15)	2411(5)	2168(4)	−1212(4)	58(1)
C(16)	2960(5)	1382(4)	−1949(3)	53(1)
C(17)	4426(5)	1590(4)	−1980(4)	59(1)
C(18)	4996(5)	886(4)	−2674(4)	64(1)
C(19)	4108(5)	−27(4)	−3372(4)	58(1)
C(20)	2659(5)	−241(5)	−3356(4)	67(1)
C(21)	2095(5)	449(5)	−2652(4)	63(1)
C(22)	3911(6)	−1500(5)	−4834(5)	76(2)
C(23)	−637(5)	3047(4)	−895(3)	52(1)
C(24)	−873(5)	2037(5)	−1903(4)	64(1)
C(25)	−1800(6)	3501(6)	−2304(4)	75(2)
C(26)	−2506(5)	4203(4)	−1699(4)	60(1)
C(27)	−2287(6)	4327(5)	−699(4)	68(1)
C(28)	−1369(6)	3753(5)	−310(4)	74(2)
C(29)	−4315(6)	5277(5)	−1595(5)	78(2)

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

Pentacarbonyl{(*Z*)-3-[(1,1-dimethylethyl)carboxy]-1-ethoxy-4,4-dimethyl-2-pentenylidene}tungsten [(*Z*)-4a] and Pentacarbonyl[1-ethoxy-4,4-dimethyl-2-pentynylidene]tungsten (6a). To 396 mg (1.00 mmol) of pentacarbonyl(1-ethoxyethylidene)tungsten (**1a**) and 303 mg (3.00 mmol) of Et_3N in 3 mL of dichloromethane/diethyl ether (1:2) are added 241 mg (2.00 mmol) of pivalic chloride (**2a**) and 10 mg of *p*-(dimethylamino)pyridine (DMAP) as a catalyst at 20 °C in an airtight 5-mL screw-top vessel with stirring. The formation of red polar (*Z*)-**4a** can be detected by TLC already after a few minutes, while $[Et_3NH]Cl$ begins to precipitate. After 2 h at 20 °C, when **1a** is consumed completely, the solvent is removed (15 Torr, 20 °C) and the residue extracted three times with 1 mL of diethyl ether each. (Fast!) chromatography on silica (column 20 × 2 cm) with pentane yields red unpolar **6a** (R_f = 0.8 in pentane, 48 mg, 10%, red oil), and with pentane/dichloromethane (4:1 to 3:1), red polar (*Z*)-**4a** [R_f = 0.5, pentane/dichloromethane (4:1), 330 mg, 59%, red crystals from diethyl ether/pentane (1:4), mp 70 °C]. A much higher yield (up to 40%) of **6a** is obtained on reaction of **1a** with *3* equiv of **2a**.

(*Z*)-**4a**: ^{1}H NMR (C_6D_6) δ 6.90 (1 H, s, 2-H), 4.55 (2 H, q, OCH_2), 1.10 (3 H, s, 3-*t*-Bu), 1.00 (3 H, t, OCH_2CH_3), 0.90 (3 H, s, OC−*t*-Bu); ^{13}C NMR (C_6D_6) δ 311.4 (W=C), 204.6 and 198.0 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 173.6 (O−CO), 150.6 (C3), 131.0 (CH, 2-C), 80.1 (OCH_2), 39.6 and 37.3 (C_q each, CMe_3 each), 27.8 and 27.4 (3 CH_3 each, *t*-Bu each), 14.9 (CH_3, Et); IR (hexane) [cm^{-1} (%)] 2068.4 (20), 1984.2 (5), 1943.3 (100) [ν(C≡O)]; IR (diffuse reflection) [cm^{-1} (%)] 1755.3 (20) [ν(OC=O)], 1612.0 (30) [ν(C=C)]; MS (70 eV) [*m*/*e* (%), ^{184}W] 564 (10) [M$^+$], 508 (5), 424 (30) [M$^+$ − 5CO], 367 (30), 337 (20), 309 (40), 266 (30), 57 (100). Anal. Calcd for $C_{19}H_{24}O_8W$ (564.2): C, 40.45; H, 4.29. Found: C, 40.68; H, 4.31.

6a: ^{1}H NMR (C_6D_6, 20 °C) δ 4.00 (2 H, s dynamically broadened, OCH_2), 1.10 (9H, s, *t*-Bu); ^{13}C NMR (C_6D_6, 20 °C) δ 290.4 (W=C), 206.1 and 198.3 [*trans*- and *cis*-CO $(CO)_5W$], 148.6 (C_q, C3), 86.0 (C_q, 76.5 (OCH_2, dynamically broadened), 29.9 (C_q, CMe_3, 29.8 (3 CH_3, *t*-Bu), 14.4 (CH_3, Et); IR (hexane) [cm^{-1} (%)] 2166.2 (20) [ν(C≡C)], 2069.9 (20), 1983.2 (5), 1954.2 (100) [ν(C≡O)]; MS (70 eV) [*m*/*e* (%), ^{184}W] 462 (10) [M$^+$], 406 (10), 378 (20), 350 (20), 320 (25) [M$^+$ −5CO], 263 (30) [320 − C_4H_9], 149 (40), 57 (100). Anal. Calcd for $C_{14}H_{14}O_6W$ (462.1): C, 36.39; H, 3.05. Found: C, 36.64; H, 3.33.

Pentacarbonyl{3-[(1-methylethyl)carboxy]-1-ethoxy-4-methyl-2-pentenylidene}tungsten [(*Z*)- and (*E*)-4b] and Pentacarbonyl{3-[(1-methylethyl)carboxy]-1-ethoxy-4-methyl-3-pentenylidene}tungsten (5b). Pentacarbonyl(1-ethoxyethylidene)tungsten (**1a**) (396 mg, 1.00 mmol) and 404 mg (4.00 mmol) of Et_3N in 3 mL of dichloromethane/diethyl ether (1:2) are reacted as described above with 320 mg (3.00 mmol) of isobutyric acid chloride (**2b**) and 10 mg of DMAP. Chromatography after 1 h, 20 °C with pentane yields a small amount of unreacted **1a**, then with pentane/dichloromethane (4:1) a red band containing (*Z*)- and (*E*)-**4b** [R_f = 0.5, pentane/dichloromethane (3:1), 290 mg, 54%, *Z*/*E* = 2:1 according to ^{1}H NMR spectra, red crystals from petane at −78 °C] followed by an orange to yellow band with **5b** [R_f = 0.4, pentane/dichloromethane (3:1); 176 mg, 33% from pentane at −78 °C, orange crystals, oil at 20 °C].

(*Z*)-**4b**: ^{1}H NMR (C_6D_6) δ 6.90 (1 H, s, 2-H), 4.53 (2 H, q, OCH_2), 2.32 (1 H, sept, OC−$CHMe_2$), 2.06 (1 H, sept, 3-$CHMe_2$), 1.06 (3 H, t, OCH_2CH_3), 1.01 [6H, d, ^3J = 7 Hz, OC−$CH(CH_3)_2$], 0.90 [6H, d, ^3J = 7 Hz, 3-$CH(CH_3)_2$]; ^{13}C NMR (C_6D_6) δ 308.4 (W=C), 204.4 and 198.0 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 172.6 (O−CO), 151.1 (C3), 132.0 (CH, 2-C), 80.0 (OCH_2), 34.4 (2 CH, 2 *i*-Pr), 19.8 and 18.9 (each 2 CH_3, 2 *i*-Pr), 14.8 (CH_3, Et); IR (hexane) [cm^{-1} (%)] 2068.7 (20), 1984.1 (5), 1943.5 (100) [ν(C≡O)]; IR (diffuse reflection) [cm^{-1} (%)] 1762.6 (20) [ν(OC=O)], 1599.1 (30) [ν(C=C)]; MS (70 eV) [*m/e* (%), ^{184}W] 536 (60) [M^+], 508 (10), 480 (20), 452 (30), 424 (40), 396 (80) [M^+ − 5CO], 367 (70), 339 (20) [396 − EtOH], 266 (60), 71 (100).

(*E*)-**4b**: ^1H NMR (C_6D_6) δ 7.36 (1 H, s, 2-H), 4.55 (2 H, q, OCH_2), 2.92 (1 H, sept, OC−$CHMe_2$), 2.28 (1 H, sept, 3-$CHMe_2$), 1.04 (3 H, t, OCH_2CH_3), 0.98 [6H, d, ^3J = 7 Hz, OC−$CH(CH_3)_2$], 0.94 [6H, d, ^3J = 7 Hz, 3-$CH(CH_3)_2$]; ^{13}C NMR (C_6D_6) δ 309.4 (W=C), 204.1 and 198.9 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 173.9 (O−CO), 156.8 (C3), 136.7 (CH, C2), 80.0 (OCH_2), 34.8 and 32.3 (2 CH, 2 *i*-Pr), 20.0, 18.9 (each 2 CH_3, 2 *i*-Pr), 14.4 (CH_3, Et); IR (hexane) [cm^{-1} (%)] 2067.4 (20), 1984.2 (5), 1943.3 (100) [ν(C≡O)]; IR (diffuse reflection) [cm^{-1} (%)] 1761.0 (20) [ν(OC=O)], 1589.1 (30 [ν(C=C)]. Anal. Calcd for $C_{17}H_{20}O_8W$ (536.2): C 38.08; H, 3.76. Found: C, 38.30; H, 3.77.

5b: ^1H NMR (C_6D_6) δ 4.50 (2 H, q, OCH_2), 3.85 (2 H, s, 2-H_2), 2.40 (1 H, sept, OC−$CHMe_2$), 1.40 and 1.35 [3 H each, s each, =$C(CH_3)_2$], 1.05 [6 H, d, ^3J = 7 Hz, OC−$CH(CH_3)_2$], 0.95 (3 H, t, OCH_2CH_3); ^{13}C NMR (C_6D_6) δ 328.6 (W=C), 203.5 and 197.8 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 174.5 (O−CO), 138.2 (C_q, C3), 122.8 (C_q, C4), 81.1 (OCH_2), 65.2 (CH_2, C2), 34.3 (CH, *i*-Pr), 19.3 and 17.5 [=$C(CH_3)_2$], 19.1 (2 CH_3, *i*-Pr), 14.4 (CH_3, Et); IR (hexane) [cm^{-1} (%)] 2070.4 (20), 1981.2 (5), 1943.4 (100) [ν(C≡O)]; IR (diffuse reflection) [cm^{-1} (%)] 1754.1 (20) [ν(OC=O)]; MS (70 eV) [*m/e* (%), ^{184}W] 536 (10) [M^+], 508 (30), 480 (5), 452 (60), 424 (40), 396 (80) [M^+ − 5CO], 366 (70), 339 (100) [396 − EtOH], 268 (60), 71 (90).

Pentacarbonyl[3-(cyclopropylcarboxy)-3-cyclopropyl-1-ethoxy-2-propenylidene]tungsten [(*Z*)- and (*E*)-4c]. Pentacarbonyl(1-ethoxyethylidene)tungsten (**1a**) (396 mg, 1.00 mmol) and 303 mg (3.00 mmol) Et_3N in 3 mL of dichloromethane are reacted as described above with 209 mg (2.00 mmol) of cyclopropanecarboxylic acid chloride (**2c**) and 10 mg of DMAP for 1.5 h at 20 °C. Chromatography with pentane/dichloromethane (3:1) yields a red band with (*Z*)- and (*E*)-**4c** [(*E*)-**4c**, R_f = 0.40; (*Z*)-**4c**, R_f = 0.35; in pentane/dichloromethane (3:1) each, *Z*/*E* = 6:1 according to integration in the ^1H NMR spectrum; separation by fractional crystallization from diethyl ether/pentane (1:3) at −15 °C. (*E*)-**4c** crystallizes first and forms orange spherical crystals, 43 mg, 8%, mp 105 °C, followed by (*Z*)-**4c** in red platelets, 239 mg, 45%, mp 77 °C].

(*Z*)-**4c**: ^1H NMR (C_6D_6) δ 7.23 (1 H, s, 2-H), 4.55 (2 H, q, OCH_2), 1.15 (1 H, m, 1′-H, OC−*c*-Pr), 1.08 (3 H, t, OCH_2CH_3), 0.86 (1 H, m, 1′-H, 3-*c*-Pr), 0.78 and 0.53 (2 H each, m each, CH_2 each, OC−*c*-Pr), 0.60 and 0.58 (2 H each, m each, CH_2 each, 3-*c*-Pr); ^{13}C NMR (C_6D_6) δ 303.1 (W=C), 204.6 and 198.3 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 170.3 (O−CO), 150.2 (C3), 133.0 (CH, C2), 80.0 (OCH_2), 16.4 (CH, C1′, OC−*c*-Pr), 14.9 (CH_3, Et), 13.0 (CH, C1′, 3-*c*-Pr), 9.4 (2 CH_2, OC−*c*-Pr), 8.0 (2 CH_2, 3-*c*-Pr); IR (hexane) [cm^{-1} (%)] 2067.4 (20), 1984.2 (5), 1943.3 (100) [ν(C≡O)]; IR (diffuse reflection) [cm^{-1} (%)] 1760.6 (20) [ν(OC=O)], 1582.7 (30) [ν(C=C)]; MS (70 eV) [*m/e* (%), ^{184}W] 532 (10) [M^+], 504 (4), 476 (4), 448 (20), 420 (30), 392 (25) [M^+ − 5CO], 337 (20), 333 (20), 266 (20), 238 (20), 149 (10), 131 (30), 69 (100). Anal. Calcd for $C_{17}H_{16}O_8W$ (532.2): C, 38.37; H, 3.03. Found: C, 38.17; H, 3.12.

(*E*)-**4c**: ^1H NMR (C_6D_6): δ 7.62 (1 H, s, 2-H), 4.53 (2 H, q, OCH_2), 2.25 (1 Hm, m, 1′-H, OC−*c*-Pr), 1.06 (1 H, m, 1′-H, 3-*c*-Pr), 0.98 (3 H, t, OCH_2CH_3), 0.82 and 0.55 (2 H each, m each, CH_2 each, OC−*c*-Pr), 0.80 and 0.32 (2 H each, m each, CH_2 each, 3-*c*-Pr); ^{13}C NMR (C_6D_6) δ 304.8 (W=C), 204.1 and 198.2 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 171.7 (O−CO), 155.7 (C3), 138.2 (CH, C2), 79.6 (OCH_2), 15.8 (CH, C1′, OC−*c*-Pr), 14.6 (CH_3, Et), 13.0 (CH, C1′, 3-*c*-Pr), 9.5 (2 CH_2, OC−*c*-Pr), 8.9 (2 CH_2, 3-*c*-Pr); IR (hexane) [cm^{-1} (%)] 2067.4 (20), 1984.2 (5), 1943.3 (100) [ν(C≡O)]; IR (diffuse reflection) [cm^{-1} (%)] 1759.1 (20) [ν(OC=O)], 1573.5 (30) [ν(C=C)]; MS (70 eV) [*m/e* (%), ^{184}W] 532 (20) [M^+], 504 (1), 448 (10), 420 (30), 392 (30) [M^+ − 5CO], 337 (40), 333 (20), 269 (20), 131 (10), 69 (100). Anal. Calcd for $C_{17}H_{16}O_8W$ (532.2); C, 38.37; H, 3.03. Found: C, 38.50; H, 3.31.

[(*Z*)-3-(Benzoyloxy)-1-ethoxy-3-phenyl-2-propenylidene]pentacarbonyltungsten [(*Z*)-4d] and [(*E*,*Z*)-5-(Benzoyloxy)-1,3-diethoxy-5-phenyl-2,4-pentadienylidene]pentacarbonyltungsten [(*E*,*Z*)-7d]. Pentacarbonyl(1-ethoxyethylidene)tungsten (**1a**) (396 mg, 1.00 mmol) and 303 mg (3.00 mmol) of Et_3N in 3 mL of dichloromethane/diethylether (1:2) are reacted as described above with 350 mg (2.50 mmol) of benzoyl chloride (**2d**) and 10 mg of DMAP for 2 h at 20 °C. Chromatography on silica yields dark-brown crystals of (*Z*)-**4d** (389 mg, 72%).[1] By extension of the reaction time to 15 h, 20 °C, only a little (*Z*)-**4d** and mainly red-brown (*E*,*Z*)-**7d** are obtained [135 mg, 40%, R_f = 0.3, in pentane/dichloromethane (3:1), red-brown crystals, mp 131 °C].

(*Z*)-**4d**: For experimental data see ref 1.

(*E*,*Z*)-**7d**: ^1H NMR (C_6D_6) δ 8.15, 7.15, and 7.05 (2:1:2; *o*-:*p*-:*m*-H, 5-benzoyloxy), 7.50, 6.95, 6.85 (2:1:2, *o*-:*p*-:*m*-H, 5-Ph), 7.08 and 7.06 (1 H each, s, 2-H and 4-H), 4.50 (2 H, q, 1-OCH_2), 3.50 (2 H, q, 3-OCH_2), 1.00 (3 H, t, 1-OCH_2CH_3), 0.50 (3 H, t, 3-OCH_2CH_3); ^{13}C NMR (C_6D_6) δ 294.5 (W=C), 204.1 and 199.2 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 163.6 (O−CO), 156.4 and 154.4 (C_q each, C3 and C5), 133.9 (CH, C2), 135.6 (2 C_q, *i*-C each, Ph), 130.6, 129.5, 129.0, 126.1 (2:3:3:2, CH each, 2 Ph); 112.1 (CH, C4), 79.3 (1-OCH_2), 65.4 (3-OCH_2), 15.0 and 13.9 (OCH_2CH_3 each); IR (hexane) [cm^{-1} (%)] 2061.2 (20), 1982.2 (5), 1933.9 (100) [ν(C≡O)]; IR (diffuse reflection) [cm^{-1} (%)] 1743.1 (20) [ν(OC=O)], 1623.3 (30) and 1511.0 (40) [ν(C=C)]; MS (70 eV) [*m/e* (%), ^{184}W] 674 (10) [M^+], 646 (40), 534 (70) [M^+ − 5CO], 506 (60), 477 (10), 344 (20), 312 (40), 245 (50), 229 (50), 215 (60), 105 (100). Anal. Calcd for $C_{27}H_{22}O_9W$ (674.3): C, 48.09; H, 3.29. Found: C, 48.36; H, 3.32.

Pentacarbonyl{(*Z*)-1-ethoxy-3-[(4-methylbenzoyl)oxy]-3-(4-methylphenyl)-2-propenylidene}tungsten [(*Z*)-4e] and Pentacarbonyl{(*E*,*Z*)-1,3-diethoxy-5-[(4-methylbenzoyl)-oxy]-5-(4-methylphenyl)-2,4-pentadienylidene}tungsten [(*E*,*Z*)-7e]. Pentacarbonyl(1-ethoxyethylidene)tungsten (**1a**) (396 mg, 1.00 mmol) and 303 mg (3.00 mmol) of Et_3N in 3 mL of dichloromethane/diethyl ether (1:2) are reacted as described above with 386 mg (2.50 mmol) of 4-methylbenzoic acid chloride (**2e**) and 10 mg of DMAP for 2 h at 20 °C to give mainly (*Z*)-**4e** , which is isolated by chromatography with pentane/dichloromethane (3:1 to 2:1) [410 mg, 65%, R_f = 0.5 in pentane/dichloromethane (3:1), brown crystals, mp 132 °C]. After 20 h at 20 °C the reaction mixture contains mainly (*E*,*Z*)-**7e**, which is isolated by chromatography with pentane/dichloromethane (1:1) [147 mg, 42%, R_f = 0.4 in pentane/dichloromethane (3:1), red-brown crystals, mp 120 °C].

(*Z*)-**4e**: ^1H NMR (C_6D_6) δ 8.10 (1 H, s, 2-H), 8.00 and 6.85 (2:2, *o*-:*m*-H, *p*-tol), 7.60 and 6.70 [2:2, *o*-:*m*-H, 3-*p*-tol], 4.50 (2 H, q, OCH_2), 1.98 and 1.90 (3 H each, 2 CH_3), 0.80 (3 H, t, OCH_2CH_3); ^{13}C NMR (C_6D_6) δ 304.8 (W=C), 204.3 and 199.0 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 163.2 (O−CO), 143.5 (C3), 145.1 and 142.0 (C_q each, C4′, *p*-tol), 132.0 (CH, C2), 130.8, 130.4, 129.9, 127.4 (each 2 CH, 2 *p*-tol); 131.7, 127.9 (C_q each, 2 *i*-C *p*-tol), 80.3 (OCH_2), 21.6 and 21.4 (each CH_3, 2 *p*-tol), 14.7 (CH_3, Et); IR (hexane) [cm^{-1} (%)] 2066.1 (20), 1981.2 (5), 1943.1 (100) [ν(C≡O)]; IR (diffuse reflection) [cm^{-1} (%)] 1744.4 (20) [ν(OC=O)], 1583.6 (30) [ν(C=C)]; MS (70 eV) [*m/e* (%), ^{184}W] 632 (1) [M^+], 604 (2), 576 (4), 548 (20), 520 (2), 492 (25) [M^+ − 5CO], 435 (30), 314 (20), 119 (100) [$MeC_6H_4CO^+$]. Anal. Calcd for $C_{25}H_{20}O_8W$ (632.3): C, 47.49; H, 3.19. Found: C, 47.48; H, 3.37.

(*E*,*Z*)-**7e**: ^1H NMR (C_6D_6) δ 8.10 and 6.90 [2:2, “d” each, 5-((4-methylbenzoyl)oxy)], 7.50 and 6.80 (2:2, “d” each, 5-tolyl); 7.20 and 7.10 (1 H each, s, 2-H and 4-H), 4.50 (2 H, q, 1-OCH_2), 3.50 (2 H, q, 3-OCH_2), 1.98 and 1.95 (3 H each, s, CH_3 each), 1.00 (3 H, t, 1-OCH_2CH_3), 0.55 (3 H, t, 3-OCH_2CH_3); ^{13}C NMR (C_6D_6) δ 293.8 (W=C), 204.1 and 199.3 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 163.7 (O−CO), 157.0 and 155.1 (C_q each, C3 and C5), 144.7 and 141.0 (C_q each, C4′ each, *p*-tol each), 133.0 (2 C_q, *i*-C each, *p*-tol), 130.8 (CH, C2), 130.1, 129.8, 126.2, 125.1

(2:2:2:2, CH each, 2 *p*-tol); 111.3 (CH, C4), 79.2 (1-OCH_2), 65.4 (3-OCH_2), 21.6 and 21.5 (CH_3 each, *p*-tol), 15.0 and 14.0 (OCH_2CH_3 each); IR (hexane) [cm^{-1} (%)] 2061.1 (20), 1983.2 (5), 1935.2 (100) [$\nu(C\equiv O)$]; IR (diffuse reflection) [cm^{-1} (%)] 1742.8 (20) [$\nu(OC{=}O)$], 1620.1 (30) and 1516.5 (40) [$\nu(C{=}C)$]; MS (70 eV) [*m/e* (%), ^{184}W] [M^+] missing. Anal. Calcd for $C_{29}H_{26}O_9W$ (702.4): C, 49.59; H, 3.73. Found: C, 49.90; H, 4.00.

Pentacarbonyl{(*Z*)-1-ethoxy-3-[(4-methoxybenzoyl)oxy]-3-(4-methoxyphenyl)-2-propenylidene}tungsten [(*Z*)-4f] and Pentacarbonyl{(*E*,*Z*)-1,3-diethoxy-5-[(4-methoxybenzoyl)oxy]-5-(4-methoxyphenyl)-2,4-pentadienylidene}tungsten [(*E*,*Z*)-7f]. Pentacarbonyl(1-ethoxyethylidene)tungsten (**1a**) 396 mg, 1.00 mmol) and 303 mg (3.00 mmol) of Et_3N in 3 mL of dichloromethane/diethyl ether (1:2) are reacted as described above with 425 mg (2.50 mmol) of 4-methoxybenzoic acid chloride (**2f**) and 10 mg of DMAP for 3 h at 20 °C. Chromatography on silica with pentane/dichloromethane (2:1) yields (*Z*)-**4f** [518 mg, 78%, $R_f = 0.5$ in pentane/dichloromethane (1:1), brown crystals, mp 126 °C]. After 1.5 days at 20 °C mainly (*E*,*Z*)-**7f** is obtained [165 mg, 45%, $R_f = 0.3$ in pentane/dichloromethane (1:1), red crystals, mp 115 °C], which is isolated by chromatography on silica with pentane/dichloromethane (1:1).

(*Z*)-**4f**: ^1H NMR (C_6D_6): δ 8.05 and 6.60 (2:2, *o-*:*m*-H, *p*-anisyl—COO), 7.60 and 6.40 [2:2, *o-*:*m*-H, 3-(*p*-anisyl)], 8.00 (1 H, s, 2-H), 4.50 (2 H, q, OCH_2), 3.15 (6H, 2 OCH_3), 0.80 (3 H, t, OCH_2CH_3); ^{13}C NMR (C_6D_6) δ 303.2 (W=C), 204.3 and 198.4 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 164.7 and 162.8 (each *C*—OCH_3), 162.9 (O—CO), 144.2 (C3), 132.9 (CH, C2), 129.3, 128.4, 115.2, 114.5 (2 CH each, 2 *p*-anisyl); 126.5, 122.0 (C_q each, 2 *i*-C *p*-anisyl), 80.3 (OCH_2), 55.2 and 55.1 (OCH_3 each, 2 *p*-anisyl), 14.7 (CH_3, Et); IR (hexane) [cm^{-1} (%)] 2064.6 (20), 1982.2 (5), 1941.4 (100) [$\nu(C\equiv O)$]; IR (diffuse reflection) [cm^{-1} (%)] 1738.8 (20) [$\nu(OC{=}O)$], 1576.6 (30) [$\nu(C{=}C)$]; MS (70 eV) [*m/e* (%), ^{184}W] 664 (1) [M^+], 636 (2), 608 (4), 580 (15), 552 (2), 524 (5) [$M^+ - 5CO$], 469 (10), 332 (10), 135 (100) [$MeOC_6H_4CO^+$]. Anal. Calcd for $C_{25}H_{20}O_{10}W$ (664.3): C, 45.18; H, 3.04. Found: C, 45.38; H, 3.15.

(*E*,*Z*)-**7f**: ^1H NMR (C_6D_6) δ 8.20 and 6.65 [2:2, each "d", 5-((4-methoxybenzoyl)oxy)], 7.50 and 6.55 (2:2, each "d", 5-*p*-anisyl), 7.20 and 7.05 (1 H each, s, 2-H and 4-H), 4.52 (2 H, q, 1-OCH_2), 3.52 (2 H, q, 3-OCH_2), 3.20 and 3.10 (3 H each, s each, OCH_3), 1.00 (3 H, t, 1-OCH_2CH_3), 0.60 (3 H, t, 3-OCH_2CH_3); ^{13}C NMR (C_6D_6) δ 293.0 (W=C), 204.2 and 199.4 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 163.3 (O—CO), 164.5 and 162.1 (C_q each, C4′ each, *p*-anisyl each), 157.4 (C_q, C3), 155.3 (C_q, C5), 132.8 (CH, C2), 127.9, 124.9, 114.9, 114.5 (2:2:2:2, each CH, 2 *p*-anisyl), 110.2 (CH, C4), 79.2 (1-OCH_2), 65.4 (3-OCH_2), 55.1 and 55.0 (OCH_3 each *p*-anisyl), 15.1 and 14.1 (OCH_2CH_3 each); IR (hexane) [cm^{-1} (%)] 2060.7 (20), 1986.7 (5), 1933.9 (100) [$\nu(C\equiv O)$]; IR (diffuse reflection) [cm^{-1} (%)] 1738.8 (20) [$\nu(OC{=}O)$], 1574.6 (30) and 1514.6 (40) [$\nu(C{=}C)$]; MS (70 eV) [*m/e* (%), ^{184}W] 734 (1) [M^+], 650 (5), 594 (20) [$M^+ - 5CO$], 566 (20), 440 (20), 135 (100) [$MeOC_6H_4CO^+$]. Anal. Calcd for $C_{29}H_{26}O_{11}W$ (734.4): C, 47.43; H, 3.57. Found: C, 47.51; H, 3.83.

Pentacarbonyl{(*Z*)-3-[(1,1-dimethylethyl)carboxy]-1-ethoxy-4,4-dimethyl-2-pentenylidene}chromium [(*Z*)-4g] and Pentacarbonyl[1-ethoxy-4,4-dimethyl-2-pentynylidene]chromium [6g]. Pentacarbonyl(1-ethoxyethylidene)chromium (**1b**) (264 mg, 1.00 mmol) and 303 mg (3.00 mmol) of Et_3N in 3 mL of dichloromethane/diethyl ether (1:2) are reacted as described above with 241 mg (2.00 mmol) of pivalic chloride (**2a**) and 10 mg of DMAP for 2 h at 20 °C. Chromatography with pentane yields red unpolar **6g** [40 mg, 12%, $R_f = 0.8$ in pentane, red oil], and with pentane/dichloromethane (4:1) red polar (*Z*)-**4g** [195 mg, 45%, $R_f = 0.5$ in pentane/dichloromethane (4:1), lit.[1]]. Reaction of **1b** with *3* equiv of **2a** leads to the formation of 30–40% of **6g**.

(*Z*)-**4g**: ^1H NMR (C_6D_6) δ 6.90 (1 H, s, 2-H), 4.60 (2 H, q, OCH_2), 1.05 (3 H, s, 3-*t*-Bu), 0.90 (3 H, t, OCH_2CH_3), 0.90 (3 H, s, OC—*t*-Bu); ^{13}C NMR (C_6D_6) δ 332.4 (Cr=C), 224.9 and 217.2 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 174.2 (O—CO), 147.9 (C3), 127.3 (CH, C2), 77.1 (OCH_2), 39.5 and 37.2 (C_q each, *C*Me_3 each), 27.6 and 27.4 (3 CH_3 each, *t*-Bu each), 14.5 (CH_3, Et); IR (hexane) [cm^{-1} (%)] 2060.8 (20), 1987.7 (5), 1945.6 (100) [$\nu(C\equiv O)$]; (diffuse reflection) [cm^{-1} (%)] 1755.0 (20) [$\nu(OC{=}O)$]; MS (70 eV) [*m/e* (%)] 432 (20) [M^+], 404 (3), 376 (5), 348 (10), 320 (10), 292 (20) [$M^+ - 5CO$], 246 (40) [292 − C_4H_8], 184 (30), 153 (40), 57 (100). Anal. Calcd for $C_{19}H_{24}CrO_8$ (432.4): C, 52.78; H, 5.59. Found: C, 53.00; H, 5.56.

6g: ^1H NMR (C_6D_6) δ 4.05 (2 H, q, OCH_2), 1.10 (9H, s, *t*-Bu); ^{13}C NMR (C_6D_6) δ 318.4 (Cr=C), 225.8 and 217.1 [*trans*- and *cis*-CO $(CO)_5Cr$], 149.4 (C_q, C3), 85.5 (C_q, C2), 75.9 (OCH_2), 30.3 (C_q, *C*Me_3), 29.8 (3 CH_3, *t*-Bu), 14.6 (CH_3, Et); IR (hexane) [cm^{-1} (%)] 2175.0 (20) [$\nu(C\equiv C)$], 2062.8 (20), 1985.6 (5), 1955.6 (100) [$\nu(C\equiv O)$]; MS (70 eV) [*m/e* (%)] 330 (20) [M^+], 274 (60), 246 (30), 218 (70), 190 (70) [$M^+ - 5CO$], 161 (20) [190 − Et], 146 (60), 144 (40) [190 − C_4H_8], 133 (70), 131 (50), 96 (80), 51 (100). Anal. Calcd for $C_{14}H_{14}CrO_6$ (330.3): C, 50.92; H, 4.27. Found: C, 51.12; H, 4.40.

Pentacarbonyl{3-[(1-methylethyl)carboxy]-1-ethoxy-4-methyl-2-pentenylidene}chromium [(*Z*)-and (*E*)-4h] and Pentacarbonyl{3-[(1-methylethyl)carboxy]-1-ethoxy-4-methyl-3-pentenylidene}chromium (5h). Pentacarbonyl(1-ethoxyethylidene)chromium (**1b**) (264 mg, 1.00 mmol) and 505 mg (5.00 mmol) of Et_3N in 3mL of dichloromethane/diethyl ether (1:2) are reacted as described above with 320 mg (3.00 mmol) of isobutyric acid chloride (**2b**) and 10 mg of DMAP for 1 h at 20 °C. Chromatography with pentane/dichloromethane (6:1 to 4:1) yields a red band with (*Z*)-**4h** [235 mg, 59%, $R_f = 0.4$ in pentane/dichloromethane (4:1), red crystals from pentane at −78 °C) and an orange-yellow band with **5h** [120 mg, 30%, $R_f = 0.3$ in pentane/dichloromethane (4:1); orange-yellow crystals from pentane at −78 °C, oil at 20 °C].

(*Z*)-**4h**: ^1H NMR (C_6D_6) δ 6.70 (1 H, s, 2-H), 4.50 (2 H, q, OCH_2), 2.40 (1 H, sept, OC—$CHMe_2$), 2.15 (1 H, sept, 3-$CHMe_2$), 1.00 (3 H, t, OCH_2CH_3), 0.95 [6H, d, $^3J = 7$ Hz, OC—$CH(CH_3)_2$], 0.80 [6H, d, $^3J = 7$ Hz, 3-$CH(CH_3)_2$]; ^{13}C NMR (C_6D_6) δ 333.6 (Cr=C), 224.8 and 217.2 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 173.2 (O—CO), 147.9 (C3), 127.9 (CH, C2), 76.9 (OCH_2), 34.4 and 33.8 (CH each, 2 *i*-Pr), 20.1 and 18.9 (2 CH_3 each, 2 *i*-Pr), 14.9 (CH_3, Et); IR (hexane) [cm^{-1} (%)] 2061.5 (20), 1987.1 (5), 1947.9 (100) [$\nu(C\equiv O)$]; IR (diffuse reflection) [cm^{-1} (%)] 1763.5 (20) [$\nu(OC{=}O)$], 1601.0 (20) [$\nu(C{=}C)$]; MS (70 eV) [*m/e* (%)] 404 (10) [M^+], 348 (20), 320 (40), 292 (70), 264 [$M^+ - 5CO$], 235 (70), 219 (80), 218 (100) [264 − C_2H_4O], 207 (60), 184 (80), 139 (95).

5h: ^1H NMR (C_6D_6) δ 4.80 (2 H, q, OCH_2), 3.98 (2 H, s, 2-H_2), 2.40 (1 H, sept, OC—$CHMe_2$), 1.50 and 1.35 [3 H each, =$C(CH_3)_2$], 1.05 [6H, d, $^3J = 7$ Hz, OC—$CH(CH_3)_2$], 0.98 (3 H, t, OCH_2CH_3); ^{13}C NMR (C_6D_6) δ 354.5 (Cr=C), 223.6 and 216.9 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 174.6 (O—CO), 144.8 (C_q, C3), 122.4 (C_q, C4), 78.4 (OCH_2), 63.2 (2 H, s, C2), 34.3 (CH, *i*-Pr), 19.3 and 17.5 [=$C(CH_3)_2$], 19.0 (2 CH_3, *i*-Pr), 14.4 (CH_3, Et); IR (hexane) [cm^{-1} (%)] 2063.1 (20), 1983.2 (5), 1948.0 (100) [$\nu(C\equiv O)$]; IR (diffuse reflection) [cm^{-1} (%)] 1746.6 (20) [$\nu(OC{=}O)$]; MS (70 eV) [*m/e* (%)] 404 (10) [M^+], 376 (20), 348 (5), 320 (40), 292 (30), 264 (60) [$M^+ - 5CO$], 217 (100) [264 − EtOH]. Anal. Calcd for $C_{17}H_{20}CrO_8$ (404.3): C, 50.50; H, 4.99. Found: C, 50.83; H, 5.21.

Pentacarbonyl[3-(cyclopropylcarboxy)-3-cyclopropyl-1-ethoxy-2-propenylidene]chromium [(*Z*)- and (*E*)-4i] and Pentacarbonyl(3-cyclopropyl-1-ethoxy-2-propynylidene)chromium (6i). Pentacarbonyl(1-ethoxyethylidene)chromium (**1b**) (264 mg, 1.00 mmol) are reacted as described above with 209 mg (2.00 mmol) of cyclopropanecarboxylic acid chloride (**2c**) and 10 mg of DMAP for 1.5 h at 20 °C. Chromatography with pentane yields red unpolar **6i** [44 mg, 11%, $R_f = 0.8$ in pentane, red oil], and with pentane/dichloromethane (3:1) a red band consisting of polar (*Z*)- and (*E*)-**4i** [232 mg, 58%, *Z*/*E* = 8:1 according to ^1H NMR spectra; $R_f(Z) = 0.40$, $R_f(E) = 0.35$, in pentane/dichloromethane (3:1) each, separation by fractional crystallization from diethyl ether/

pentane (1:3) at −15 °C; (*E*)-**4i** is obtained first and forms orange spherical crystals, mp 76 °C, while (*Z*)-**4i** forms red needles, mp 65 °C]. Reaction of **1b** with *3* equiv of **2c** leads to the formation of 25−40% of **6i**.

(*Z*)-**4i**: ^{1}H NMR (C_6D_6) δ 7.05 (1 H, s, 2-H), 4.70 (2 H, q, OCH_2), 1.20 (1 H, m, 1′-H, OC−*c*-Pr), 1.10 (3 H, t, OCH_2CH_3), 0.89 (1 H, m, 1′-H, 3-*c*-Pr), 0.80 and 0.45 (2 H each, m each, CH_2 each, OC−*c*-Pr), 0.63 and 0.48 (2 H each, m each, CH_2 each, 3-*c*-Pr); ^{13}C NMR (C_6D_6) δ 331.5 (Cr=C), 224.6 and 217.4 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 170.7 (O−CO), 146.2 (C3), 129.8 (CH, C2), 77.2 (OCH_2), 15.9 (CH, C1′, OC−*c*-Pr), 15.0 (CH_3, Et), 13.0 (CH, C1′, 3-*c*-Pr), 9.4 (2 CH_2, OC−*c*-Pr), 7.7 (2 CH_2, 3-*c*-Pr); IR (hexane) [cm^{-1} (%)] 2059.3 (40), 1983.5 (5), 1945.1 (100) [ν(C≡O)]; IR (diffuse reflection) [cm^{-1} (%)] 1759.8 (20) [ν(OC=O)], 1585.9 (30) [ν(C=C)]; MS (70 eV) [*m*/*e* (%)] 400 (20) [M$^+$], 372 (5), 344 (20), 316 (10), 288 (10), 260 (20) [M$^+$ − 5CO], 258 (60), 137 (60), 69 (100). Anal. Calcd for $C_{17}H_{16}CrO_8$ (400.3): C, 51.01; H, 4.03. Found: C, 50.88; H, 4.09.

(*E*)-**4i**: ^{1}H NMR (C_6D_6) δ 7.50 (1 H, s, 2-H), 4.65 (2 H, q, OCH_2), 2.05 (1 H, m, 1′-H, OC−*c*-Pr), 1.16 (1 H, m, 1′-H, 3-*c*-Pr), 1.00 (3 H, t, OCH_2CH_3), 0.87 and 0.65 (2 H each, m each, CH_2 each, OC−*c*-Pr), 0.78 and 0.52 (2 H each, m each, CH_2 each, 3-*c*-Pr); ^{13}C NMR (C_6D_6) δ 328.5 (Cr=C), 224.7 and 217.4 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 170.4 (O−CO), 148.3 (C3), 134.2 (CH, C2), 77.1 (OCH_2), 15.2 (CH, C1′, OC−*c*-Pr), 15.0 (CH_3, Et), 13.1 (CH, C1′, 3-*c*-Pr), 9.5 (2 CH_2, OC−*c*-Pr), 8.7 (2 CH_2, 3-*c*-Pr); IR (hexane) [cm^{-1} (%)] 2059.3 (40), 1984.1 (5), 1945.1 (100) [ν)C≡O)]; IR (diffuse reflection) [cm^{-1} (%)] 1757.1 (20) [ν(OC=O)], 1574.7 (30) [ν(C=C)]; MS (70 eV) [*m*/*e* (%)] 400 (20) [M$^+$], 372 (5), 344 (20), 316 (10), 288 (10), 260 (20) [M$^+$ − 5CO], 258 (60), 137 (60), 69 (100). Anal. Calcd for $C_{17}H_{16}CrO_8$ (400.3): C, 51.01; H, 4.03. Found: C, 51.10, H, 4.04.

6i: ^{1}H NMR (C_6D_6) δ 3.90 (2 H, q, OCH_2), 1.09 (1 H, m, CH, *c*-C_3H_5), 0.88 and 0.57 (2 H each, m each, 2 CH_2, *c*-C_3H_5), 0.90 (3 H, t, CH_3, Et); ^{13}C NMR (C_6D_6) δ 315.2 (Cr=C), 225.4 and 217.2 [*trans*- and *cis*-CO, $(CO)_5Cr$], 149.5 (C_q, C3), 83.4 (C_q, C2), 75.9 (OCH_2), 14.5 (CH_3, Et), 14.4 (CH, *c*-C_3H_5), 12.8 (2 CH_2, *c*-C_3H_5); IR (hexane) [cm^{-1} (%)] 2157.2 (10) [ν(C≡C)], 2061.1 (30), 1990.5 (5), 1959.2 (100) [ν(C≡O)]; MS (70 eV) [*m*/*e* (%)] 314 (20) [M$^+$], 258 (40), 230 (40), 202 (30), 174 (80) [M$^+$ − CO], 146 (80), 71 (90), 69 (90), 57 (100). Anal. Calcd for $C_{13}H_{10}CrO_6$ (314.2): C, 49.69; H, 3.21. Found: C, 49.87; H, 3.42.

[(*Z*)-3-(Benzoyloxy)-1-ethoxy-4-phenyl-2-propenylidene]pentacarbonylchromium [(*Z*)-4k]. Pentacarbonyl(1-ethoxyethylidene)chromium (**1b**) (264 mg, 1.00 mmol) and 303 mg (3.00 mmol) of Et_3N in 3 mL of dichloromethane/diethyl ether (1:2) are reacted as described above with 350 mg (2.50 mmol) of benzoyl chloride (**2d**) and 10 mg of DMAP for 1.5 h at 20 °C. Chromatography on silica with pentane yields dark-brown crystals of (*Z*)-**4k** (321 mg, 68%). For experimental data see ref 1.

Pentacarbonyl{(*Z*)-1-ethoxy-3-[(4-methoxybenzoyl)oxy]-3-(4-methoxyphenyl)-2-propenylidene}chromium [(*Z*)-4l]. Pentacarbonyl(1-ethoxyethylidene)chromium (**1b**) (264 mg, 1.00 mmol) and 303 mg (3.00 mmol) of Et_3N in 3 mL of dichloromethane/diethyl ether (1:2) are reacted as described above with 425 mg (2.50 mmol) of 4-methoxybenzoic acid chloride (**2f**) and 10 mg of DMAP for 4 h at 20 °C. Chromatography with pentane/dichloromethane (2:1) yields (*Z*)-**4l** [R_f = 0.5, in pentane/dichloromethane (1:1), black crystals]. ^{1}H NMR (C_6D_6): δ 8.05 and 6.60 (2:2, *o*-:*m*-H, *p*-anisyl−COO), 7.60 and 6.45 [2:2, *o*-:*m*-H, 3-(*p*-anisyl)], 7.95 (1 H, s, 2-H), 4.60 (2 H, q, OCH_2), 3.15 and 3.10 (3 H each, 2 OCH_3), 0.95 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 331.0 (Cr=C), 224.8 and 217.5 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 164.7 and 162.7 (C−OCH_3 each), 163.2 (O−CO), 140.6 (C3), 132.8 (CH, C2), 129.3, 127.4, 115.1, 114.5 (2 CH each, 2 *p*-anisyl), 126.4 and 122.0 (C_q each, 2 *i*-C *p*-anisyl), 77.5 (OCH_2), 55.1 and 55.0 (OCH_3 each, 2 *p*-anisyl), 14.9 (CH_3, Et). IR (hexane) [cm^{-1} (%)]: 2058.8 (60), 1986.5 (5), 1946.9 (100) [ν(C≡O)]; (diffuse reflection) 1738.0 (20) [ν(OC=O)], 1577.2 (30) [ν(C=C)]. MS (70 eV), *m*/*e* (%): 532 (1) [M$^+$], 420 (10), 392 (20) [M$^+$ − 5CO], 348 (20), 335 (20), 280 (10), 240 (20), 51 (100). Anal. Calcd for $C_{25}H_{20}CrO_{10}$ (532.4): C, 56.40; H, 3.79. Found: C, 56.38; H, 3.95.

Pentacarbonyl[1-ethoxy(7-oxo-2-benzofuranylidene)ethylidene]tungsten [(*Z*)-4m]. Pentacarbonyl(1-ethoxyethylidene)tungsten (**1a**) (396 mg, 1.00 mmol) and 303 mg (3.00 mmol) of Et_3N in 3 mL of dichloromethane are reacted as described above with 203 mg (1.00 mmol) of *o*-phthalic acid dichloride (**2m**) and 10 mg of DMAP for 4 h at 20 °C. Chromatography on silica yields (*Z*)-**4m** [248 mg, 54%, brown crystals]. ^{1}H NMR (C_6D_6): δ 7.30, 7.10, 6.70 (1:1:2, *o*-benzofuranyl), 4.60 (2 H, q, OCH_2), 1.10 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 301.8 (W=C), 204.0 and 198.1 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 167.0 (O−CO), 148.0 and 142.3 (C_q each, benzofuranyl), 139.9 (C3), 132.2 (CH, C2), 134.7, 126.2, 121.6, 120.3 (CH each, benzofuranyl), 80.5 (OCH_2), 14.9 (CH_3, Et). IR (hexane), cm^{-1} (%): 2065.1 (25), 1981.5 (5), 1944.3 (100) [ν(C≡O)]. Anal. Calcd for $C_{17}H_{10}O_8W$ (526.1): C, 38.81; H, 1.92. Found: C, 38.94; H, 2.23.

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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 figures showing the structure and crystal packing of the complex (8 pages). Ordering information is given on any current masthead page.

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