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Novel Phosphonium Allenide and 2-Phosphanylethenyl Carbene Chromium and Tungsten Complexes

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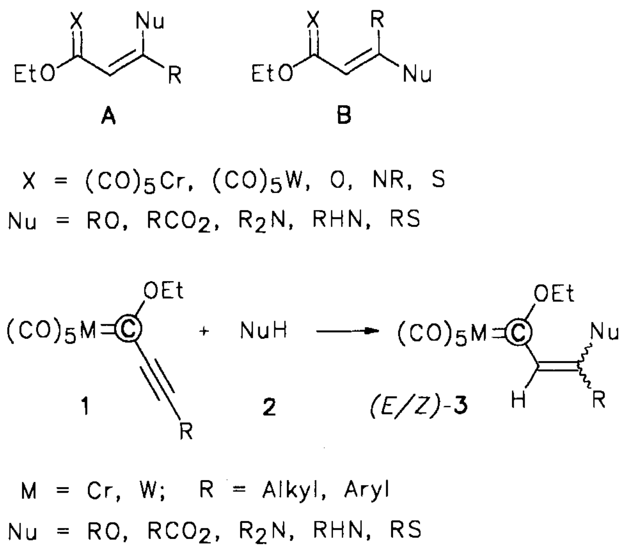
Alkynylcarbene complexes $(CO)_5M{=}C(OEt){-}C{\equiv}C{-}R$ **1** (M = Cr, W; R = Ph, *t*Bu, $SiMe_3$) readily add *tertiary* phosphanes $PPhR'_2$ **4** (R' = Ph, Me) to form stable zwitterionic phosphonium allenide complexes $(CO)_5M^-{-}C(OEt){=}C{=}C(R){-}P^+PhR'_2$ **5**. Complex **5a** (M = Cr, R = R' = Ph) was characterized by X-ray diffraction. The addition of *secondary* phosphanes PHR_2 **6** to **1** affords red (2-phosphanyl ethenyl)carbene complexes $(CO)_5M{=}C(OEt){-}CH{=}C(R){-}PR_2$ (*E*)-**8** (R = *t*Bu, cC_6H_{11}, Ph) in 34–89% isolated yields. Dinuclear complexes $(CO)_5M{=}C(OEt){-}CH{=}C(R){-}P(R_2)M(CO)_5$ (*E*)-**9** are obtained as byproducts. Compounds (*E*)-**8b** (M = Cr, R = cC_6H_{11}) and (*E*)-**9i** (M = Cr, R = Ph) were characterized by X-ray analyses.

Following the first synthesis of metal carbene complexes by *E. O. Fischer*[2], these compounds have become of much interest to organic chemists within the past 15 years as building blocks for organic synthesis[3–9], alkenylcarbene complexes $(CO)_5M{=}CX{-}CR{=}CR_2$ (M = Cr, W) having gained most attention in this respect. Carbene complexes of this type were obtained as early as 1967[10], and since then they have been shown to exhibit a very rich chemistry. These compounds may react as ester analogues, due to the isolobal relationship[11], as well as participate in many other reactions not related to ester chemistry. Up to date a wide variety of keto ester equivalents $(CO)_5M{=}C(OEt){-}CH{=}C(Nu)R$ **A**, **B** (M = Cr, W) are available, which comprise enamines (Nu = R_2N[12,13,14], RHN[15], H_2N[13,15]), enol ethers (Nu = RO[13,14,16,17]), enol esters (Nu = RCO_2[17]), and thioenol ethers (Nu = RS[13]). Several routes are known for the preparation of such compounds[18], one of which involves the addition of protic nucleophiles to alkynylcarbene complexes **1** (Scheme 1)[12,19].

Allene-Type Phosphorus Ylide Ligands

In earlier studies concerning the mechanism of Michael-analogous additions to alkynylcarbene complexes, we and others postulated a two-step process involving the intermediacy of allene-type complexes[13,15,16,17,20]. We now present unambiguous structural evidence of such intermediates by isolation of zwitterionic adducts of phosphanes **4** to alkynylcarbene complexes **1** (Scheme 2).

Scheme 1. Ethenylcarbene complexes **3** and keto ester equivalents **A**, **B**



X = (CO)5Cr, (CO)5W, O, NR, S
Nu = RO, RCO2, R2N, RHN, RS

M = Cr, W; R = Alkyl, Aryl
Nu = RO, RCO2, R2N, RHN, RS

It is well-known that reactions of electron-deficient alkynes, e.g. acetylenedicarboxylic esters, with one equivalent of triphenylphosphane give zwitterionic intermediates[21], which are unstable, but can be trapped at low temperatures by carbon dioxide or excess triphenylphosphane[22,23]. The addition of phosphanes **4** to electron-deficient C≡C bonds of **1** leads to the formation of 1:1 adducts **5**. These separate from hexane solution as yellow crystals in 93–98% yield (Table 1) and are stable at 20°C in the solid state, but redis-

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[+] Crystal structure analysis.

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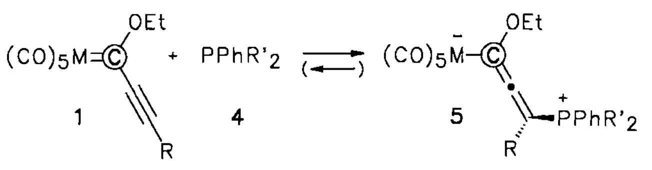
sociate in solution, at least to some extent. NMR spectra of **5a**, **b**, **d**–**f** (R = Ph, $SiMe_3$) at 20°C, 360 MHz, as well as IR spectra in hexane do not indicate any dissociation, but NMR spectra of **5c** (R = *t*Bu) show signals of the starting components **1b** and **4a** at 20°C, and the "frozen" spectrum of the adduct **5c** appears only at −30°C (Table 1).

Scheme 2. Phosphonium allenide adducts **5** from *tertiary* phosphanes and **1**



1	M	R	4	R'
a	Cr	Ph	a	Ph
b	Cr	*t*Bu	b	Me
c	W	Ph		
d	W	$SiMe_3$		

Numbering of **5** see Table 1

Table 1. Yields of **5** and selected $^{13}C(^1H)$-NMR shifts[a], ^{31}P-^{13}C (absolute) coupling constants[b] and IR vibrations[c] of **5** and **1**

	M	R	R'	δC1	δC2	δC3	δOCH_2	^3J(P-C1)	^2J(P-C2)	^1J(P-C3)
1a	Cr	Ph	-	314.1	91.9	121.1	75.8	-	-	-
1b	Cr	*t*Bu	-	318.4	85.5	149.4	75.9	-	-	-
1c	W	Ph	-	286.1	97.2	130.0	75.8	-	-	-
5a	Cr	Ph	Ph	196.8	160.0	75.5	70.8	13.1	13.1	96.0
5b	Cr	Ph	Me	190.5	158.0	75.0	71.3	13.1	13.1	96.0
5c	Cr	*t*Bu	Ph	204.2	159.6	83.8	69.8	12.6	13.7	76.0
5d	W	Ph	Ph	204.0	150.0	75.6	70.3	13.0	13.1	96.0
5e	W	Ph	Me	198.7	148.1	76.0	71.0	13.0	13.1	96.0
5f	W	$SiMe_3$	Ph	212.7	139.6	65.3	69.3	13.0	17.4	47.9

	δOCH_2	ν(C≡C)	ν(C≡O) and ν(C=C=C) resp.	**5**[%]
1a	4.70	2154(5)	A: 2062(25), 1985(4), 1967(100)	-
1b	4.05	2175(20)	A: 2063(20), 1986(5), 1956(100)	-
1c	4.65	2156(20)	A: 2069(20), 1987(5), 1959(100)	-
5a	3.60 and 3.30	-	A: 2044(20),1949(30),1913(100),1873(40) B: 2042(55),1960(40),1901(100),1872(90)	98
5b	3.61	-	A: 2044(20),1963(10),1912(100),1878(40) B: 2043(50),1963(30),1905(100),1880(60)	93
5c	3.51 and 3.35	-	A: signals of **1b**, due to dissociation B: 2041(55),1952(40),1900(100),1869(80)	94
5d	3.60 and 3.25	-	A: 2054(20),1976(30),1911(100),1873(40) B: 2052(50),1960(40),1900(100),1866(90)	97
5e	3.61	-	A: 2056(20),1975(30),1917(100),1845(40) B: 2055(10),1974(40),1913(100),1850(60)	94
5f	3.50 and 3.05	-	B: 2052(40),1957(30),1917(100),1869(90)	90

[a] In C_6D_6 at 20°C except for **5c** in CD_3COCD_3 at −30°C; chemical shifts relative to TMS, δ scale. – [b] In Hz. – [c] In cm^{-1}, intensity in brackets; A: in hexane, B: diffuse reflection.

The formation of adducts **5** from **1** and **4** involves characteristic changes in the NMR and IR spectra. These comprise strong upfield shifts of the signals of carbon C1 (M = Cr, by 114–124 ppm; M = W, by 82–86) and C3 (by 46–65 and 55 ppm) as well as downfield shifts of the C2 signals (by 68–74 and 51–53 ppm) due to the transformation of the alkynylcarbene into an allenide moiety (Table 1). Interestingly, the ^{13}C shifts δ(Cr=C) are similar to those observed in the spectra of structurally related zwitterionic 2-azoniaallenyl complexes **G**[24] (Scheme 3, M = Cr). The assignment of chemical shifts of the allenide unit is based on the ^{31}P-^{13}C coupling pattern, in which the presence of a positively charged phosphorus is indicated by a strong ^1J coupling[25]. ^1J(P,C3) (**5a**: 96 Hz) lies within the same order of magnitude as ^1J(P,*i*C) of the 3-Ph group (**5a**: 82.8 Hz). Strong bathochromic shifts of the ν(C≡O) bands in the IR spectra of **5** as compared to **1** are observed, which point to an accumulation of negative charge on the metal moiety[26] in line with the proposed zwitterionic nature of the molecules. The ^1H signals of the OCH_2 groups are shifted upfield and exhibit remarkable shift differences due to the chirality induced by the allenide unit.

Crystal-Structure Analysis of 5a

Figure 1 shows the molecular structure and Table 3 compiles the data of the X-ray structure analysis of **5a**. The compound forms orthorhombic crystals in the space group *Pbca*. The coordination plane of the ylide carbon atom approximately bisects the angle between two cisoid CO groups at the chromium atom (C1–Cr1–C6–C9 −30.9°). The coordination sphere of the phosphorus atom is essentially tetrahedral. The four P1–C distances are found within a narrow range of 1.79–1.80 Å. The allene unit is slightly bent (C10–C9–C6 171.9°, torsion angles Cr1–C6–C9–C10 17.4 and C6–C9–C10–P1 −118.7°) but its terminal carbon atoms are coordinated essentially planar (sum of bond angles 360.0 and 360.1°). The distance C9–C10 of 1.340(3) Å of the allene portion is within the range found in many organic conjugated diene systems (see e.g. 1,3-butadiene, C1–C2 1.330, C2–C3 1.455 Å), while the C6–C9 distance of 1.287(3) Å is somewhat shortened. Due to the delocalization of charge to the metal unit the Cr1–C5 distance is shorter than that of Cr1–C1 by 0.04 Å, and the C5–O5 distance is somewhat longer than that of C1–O1 by 0.01 Å. A small deviation from linearity is observed with C5–Cr1–C6 173.0°.

Compounds **5** contain a novel type of ligand based on a phosphonium allenide **C** structure (Scheme 3). A coordination of **C** by the ylide carbon atom of the alkynylphosphorane structure **D** could be an alternative coordination mode, which would lead to the formation of complexes **E**. The latter can be excluded on the basis of the chemical shifts of the NMR signals as well as on the absence of ν(C≡C) bands in the solid-state IR spectra of **5**. The formation of 1-adducts **F** of **4** to **1** has not been observed, though similar adducts of (less bulkier) phosphanes to carbene carbons of other carbene complexes are well known[26].

(2-Phosphanylethenyl)carbene Complexes (*E*)-8 and (*E*)-9

In contrast to the reaction of tertiary phosphanes **4** with alkynylcarbene complexes **1**, which gives stable zwitterionic compounds **5**, adducts **7** from *secondary* phosphanes **6** and **1** could not be isolated. It seems reasonable to assume that adducts **7** are formed initially, but rearrange fast by hydro-

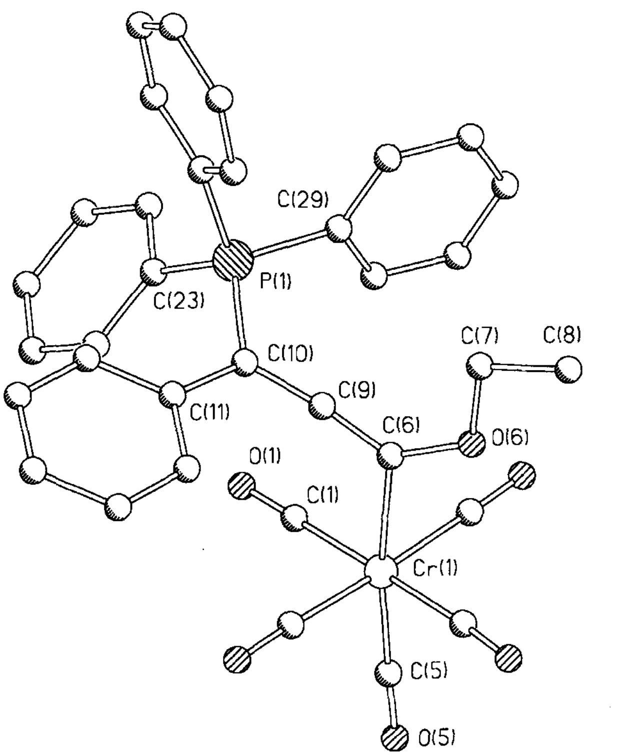
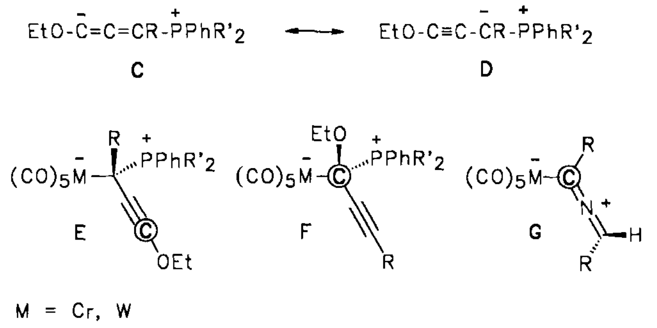


Figure 1. Molecular structure of **5a** with selected bond lengths [Å] and angles [°]: Cr(1)–C(5) 1.842(3), Cr(1)–C(1) 1.881(3), Cr(1)–C(6) 2.150(2), P(1)–C(10) 1.792(2), O(1)–C(1) 1.148(3), O(5)–C(5) 1.162(3), O(6)–C(6) 1.376(2), C(6)–C(9) 1.287(3), C(9)–C(10) 1.340(3), C(10)–C(11) 1.486(3); C(5)–Cr(1)–C(6) 172.96(10), C(1)–Cr(1)–C(6) 93.07(10), C(10)–P(1)–C(29) 109.52(10), C(6)–O(6)–C(7) 115.8(2), C(9)–C(6)–O(6) 124.1(2), C(9)–C(6)–Cr(1) 121.1(2), O(6)–C(6)–Cr(1) 114.8(2), C(6)–C(9)–C(10) 171.9(2), C(9)–C(10)–C(11) 123.0(2), C(9)–C(10)–P(1) 115.8(2), C(11)–C(10)–P(1) 121.3(2)

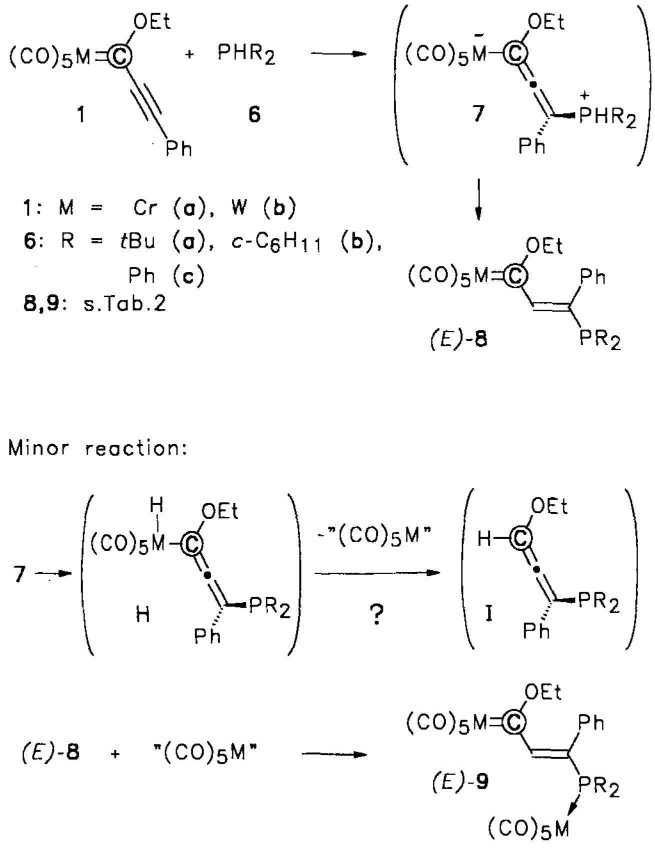
Scheme 3. Phosphonium allenide and alkynylphosphorane ligands **C** and **D**



gen migration and thus give (2-phosphanylethenyl)carbene complexes (*E*)-**8** as the main products (Scheme 4). The latter are isolated in yields up to 89% as red crystals (Table 2). Small amounts of dinuclear (2-phosphanylethenyl)carbene complexes (*E*)-**9** are also obtained. They apparently are generated by a transmetalation process, which may be induced by a proton transfer from the phosphorus atom of **7** to the metal, and a subsequent reductive elimination of an allene unit **I**.

The ^{13}C-NMR spectra of (*E*)-**8** exhibit strong downfield shifts of the signals of C1 (Table 2), which are typical of carbene complexes [δ(Cr=C): 337–339, δ(W=C): 309–312]. The phosphorus coupling to C3 is much bigger (^{1}J = 39–45 Hz) than to C2 (^{2}J = 2–9 Hz). The resonance signal of 2-H appears as a singlet at δ = 7.28–7.85, which is slightly broadened by a small {P,H} coupling. The ν(C≡O) bands in the IR spectra indicate the presence of a $(CO)_5M$ unit. They are shifted to higher frequencies (Table 2) than in the corresponding (2-aminoethenyl)carbene complexes [e.g. $(CO)_5Cr{=}C(OEt){-}CH{=}C(NMe_2)Ph$: ν(C≡O) 2048, 1982, 1928 cm^{-1}][27]. A most characteristic spectroscopic feature is the strong increase of ^{3}J(P,2-H) observed in the ^{1}H-NMR spectra of (*E*)-**9** [(*E*)-**8**: ^{3}J(P,2-H) < 1 Hz; (*E*)-**9**: 13–15] as a direct consequence of the quaternization of the phosphorus by coordination with a metal atom.

Scheme 4. (2-Phosphanylethenyl)carbene complexes (*E*)-**8** and (*E*)-**9** formed by addition of *secondary* phosphanes **6** to **1**



Crystal Structures of (*E*)-8b and (*E*)-9i

(2-Phosphanylethenyl)carbene complexes of type **8** apparently have not been obtained before[28]. In order to gain more detailed insight into the molecular structure of such compounds, X-ray structure-analyses of (*E*)-**8b** and (*E*)-**9i** were performed. Figure 2 shows the molecular structure and Table 3 compiles the data of the X-ray structure analyses. Compound (*E*)-**8b** forms monoclinic crystals in the space group $P2_1/n$. The coordination plane of the carbene carbon atom approximately bisects the angle between two cisoid CO groups at the chromium atom (C1–Cr1–C6–C9 30.9°). The distances Cr1–C6 = 2.044(2) Å, C6–O6 =

Table 2. Selected $^{13}C(^{1}H)$-NMR shifts[a], ^{31}P-^{13}C coupling constants[b], IR vibrations[c], and isolated yields of (*E*)-**8** and (*E*)-**9**

	M	R	*C*1	*C*2	*C*3	O*C*H$_2$	^1J(P-C3)	^2J(P-C2)	^3J(P-C1)
8g	Cr	*t*Bu	339.0	149.3	143.6	76.8	45	2	0
8h	Cr	Cy	336.7	146.1	143.4	76.8	37	7	0
8i	Cr	Ph	338.6	147.0	141.8	76.2	39	9	0
8k	W	*t*Bu	311.7	153.0	146.4	79.3	43	3	0
8l	W	Cy	309.3	149.5	147.2	79.1	39	5	0
9g	Cr	*t*Bu	-	-	-	-	-	-	-
9h	Cr	Cy	341.3	154.9	134.3	77.6	11	13	0
9i	Cr	Ph	343.5	150.6	134.0	77.4	27	11	0
9k	W	*t*Bu	316.0	160.2	138.7	79.9	25	12	6

	OC*H*$_2$	2-H	^3J(P,H)	ν(C≡O) (%)	[%]
8g	4.25	7.85	0	2056.4 (20), 1985.6 (5), 1944.7 (100)	89
8h	4.35	7.60	0	2055.9 (25), 1983.3 (5), 1942.9 (100)	77
8i	4.28	7.28	0	2059.5 (25), 1987.9 (5), 1945.3 (100)	34
8k	4.15	7.77	0	2064.5 (40), 1982.3 (5), 1942.6 (100)	89
8l	4.20	7.55	0	2064.3 (25), 1974.1 (5), 1941.4 (100)	67
9g	4.20	8.05	14.0	2057.6 (20), 1983.0 (5), 1946.6 (100) 2064.8 (30), 1930.3 (70)	5
9h	4.30	8.10	15.2	2057.8 (20), 1983.3 (5), 1947.9 (100) 2063.5 (30), 1929.1 (80)	7
9i	4.20	7.93	15.5	2059.9 (25), 1984.3 (5), 1952.8 (100) 2065.6 (20), 1936.5 (80)	9
9k	4.05	7.85	13.5	2068.2 (20, broad), 1982.3 (5), 1937.8 (100 broad)	5

[a] In C_6D_6, chemical shifts relative to TMS. – [b] In Hz. – [c] In hexane; cm^{-1}, intensities in brackets.

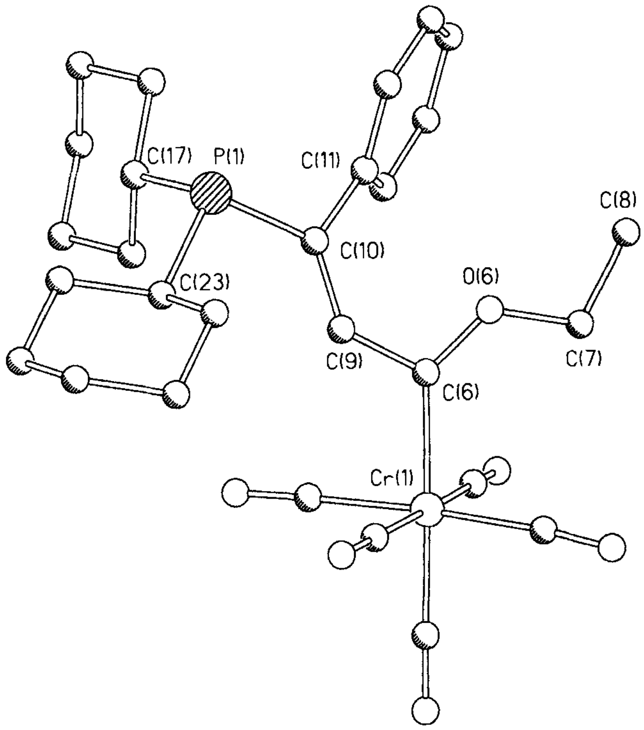


Figure 2. Molecular structure of (*E*)-**8b** with selected bond lengths [Å] and angles [°]: Cr(1)−C(2) 1.879(3), Cr(1)−C(1) 1.890(3), Cr(1)−C(3) 1.893(3), Cr(1)−C(6) 2.044(2), P(1)−C(10) 1.841(2), P(1)−C(23) 1.853(3), P(1)−C(17) 1.868(3), O(1)−C(1) 1.139(3), O(2)−C(2) 1.140(3), O(6)−C(6) 1.314(3), C(6)−C(9) 1.474(3), C(9)−C(10) 1.340(3), C(10)−C(11) 1.488(3); C(2)−Cr(1)−C(6) 178.72(12), C(1)−Cr(1)−C(6) 89.44(11), C(10)−P(1)−C(23) 103.45(11), C(10)−P(1)−C(17) 101.80(11), C(23)−P(1)−C(17) 104.42(12), O(6)−C(6)−C(9) 107.4(2), O(6)−C(6)−Cr(1) 132.3(2), C(9)−C(6)−Cr(1) 120.3(2), C(10)−C(9)−C(6) 128.6(2), C(9)−C(10)−C(11) 124.0(2), C(9)−C(10)−P(1) 123.4(2), C(11)−C(10)−P(1) 112.6(2), C(22)−C(17)−P(1) 115.7(2), C(18)−C(17)−P(1) 112.9(2)

1.314(3), and C6−C9 = 1.474(3) are similar to those observed in $(CO)_5Cr{=}C(OEt)Ph$ (2.04, 1.33, and 1.47 Å)[29]. The 1-chroma-1,3-diene unit adopts a *s-trans* configuration (torsion angle Cr1−C6−C9−C10 17.4°), in which the C=C bond is essentially planar (torsion angle C6−C9−C10−P1 −118.7°). There are no significant deviations between the distances of the *trans*-CO and the *cis*-CO groups [Cr1−C2 1.879(3) Å, Cr1−C1 1.890(3)], which indicates little or no charge delocalization from the carbene carbon to the metal unit.

The geometry of (*E*)-**9i** (Figure 3) is similar to that of (*E*)-**8b**. As a consequence of the coordination of Cr(2) to the P(1) of (*E*)-**8b** the P(1)−C(10) and also the Cr=C distance become slightly shorter in (*E*)-**9i**. The O6−C6 distance is shortened by 0.15 Å as compared to O6−C7 distance, due to a resonance interaction with the carbene carbon atom. The coordination geometry at the phosphorus shows significant deviations from a tetrahedral configuration.

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Experimental

All operations were performed under argon. Solvents were distilled from sodium/benzophenone. – ^1H and ^{13}C NMR: Bruker WM 300. Multiplicities were determined by DEPT. Chemical shifts refer to $\delta_{TMS} = 0.00$. Coupling constants *J*(P,C) and *J*(P,H) in Hz and absolute values. – IR: Digilab FTS 45. – MS: Finnigan MAT 312. – Elemental analyses: Perkin Elmer 240 elemental analyzer. – Melting points: uncorrected. – Column chromatography: Merck-Kieselgel 100. – TLC: Merck DC-Alufolien Kieselgel 60 F 254. R_f values refer to TLC tests.

Pentacarbonyl[1-ethoxy-3-phenyl-3-(triphenylphosphonio)-1,2-propadienide]chromium (**5a**): 350 mg (1.00 mmol) of pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)chromium (**1a**) is added to 262 mg (1.00 mmol) of triphenylphosphane (**4a**) in 3 ml of pentane with vigorous stirring at 20°C in a centrifuge tube. Compound **5a** separates as yellowish crystals which are collected and washed twice with 3 ml of pentane each; yield: 602 mg (98%), m.p. 122°C. – ^1H NMR (C_6D_6): δ = 7.80, 6.95, 6.85 (6:3:6H, m each, PPh_3); 7.60, 6.90, 6.85 (2:2:1H, m each, 3-Ph); 3.60 and 3.30 (1H each, m each, diastereotopic OCH_2), 1.15 (3H, CH_2CH_3). – ^{13}C NMR ($CDCl_3$): δ = 226.2 and 220.3 [1:4, *trans*- and *cis*-CO, $(CO)_5Cr$], 196.8 [C(q), d, ^3J(P,C) = 13.1 Hz, C1], 160.0 [C(q), d, ^2J(P,C) = 13.1 Hz, C2], 134.5 [C(q), d, ^2J(P,C) = 17.5 Hz, 3-Ph], 134.8 (CH, C4′, PPh), 134.5 [CH, d, ^3J(P,C) = 8.5 Hz, PPh], 129.8 [CH, d, ^2J(P,C) = 13.1 Hz, PPh]; 128.3, 127.3, 125.8 (CH each, 2:2:1, 3-Ph); 124.4 [C(q), d, ^1J(P,C) = 82.8 Hz, C1′, PPh], 75.5 [C(q), d, ^1J(P,C) = 96.0 Hz, C3], 70.8 (OCH_2), 15.6 (CH_3, OEt). – IR (hexane), (%): ṽ = 2044.2 cm^{-1} (20), 1949.3 (30), 1913.3 (100), 1873.2

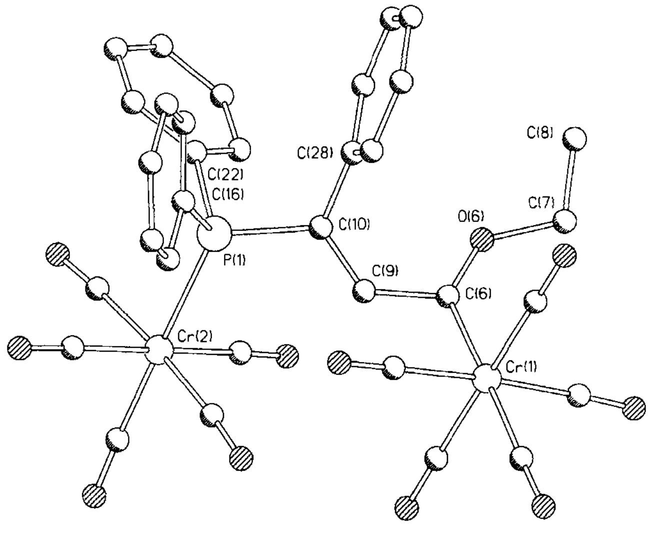

Figure 3. Molecular structure of (*E*)-**9i** with selected bond lengths [Å] and angles [°]: Cr(1)−C(6) 2.020(3), O(6)−C(6) 1.316(3), O(6)−C(7) 1.462(3), C(6)−C(9) 1.490(4), C(9)−C(10) 1.337(4), P(1)−C(10) 1.857(3), Cr(2)−P(1) 2.4094(8), P(1)−C(22) 1.829(3), P(1)−C(16) 1.831(3), C(10)−C(28) 1.496(3); C(22)−P(1)−C(16) 107.18(13), C(22)−P(1)−C(10) 102.83(12), C(16)−P(1)−C(10) 98.37(12), C(22)−P(1)−Cr(2) 108.03(9), C(16)−P(1)−Cr(2) 119.13(9), C(10)−P(1)−Cr(2) 119.61(9), C(6)−O(6)−C(7) 123.4(2), O(6)−C(6)−C(9) 106.3(2), O(6)−C(6)−Cr(1) 133.4(2), C(9)−C(6)−Cr(1) 120.3(2), C(10)−C(9)−C(6) 124.8(2), C(9)−C(10)−C(28) 122.1(2), C(9)−C(10)−P(1) 119.6(2)

Table 3. Crystal data and structure refinement for **5a**, (*E*)-**8h**, and (*E*)-**9i**. Further details of the crystal structure may be requested from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, F.R.G., on quoting the depository number CSD-58269, the name of the authors, and the journal citation

Compound	**5a**	(*E*)-**8h**	(*E*)-**9i**
Empirical formula	$C_{34}H_{25}CrO_6P$	$C_{28}H_{33}O_6PCr$	$C_{33}H_{21}O_{11}PCr_2$
Formula weight	612.51	548.5	364.23
Temperature [K]	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	triclinic
Space group	*P*bca	$P2_1/n$	P1
Unit cell dimensions			
a [Å]	18.302 (4)	14.915(3)	11.164(1)
b [Å]	16.228 (4)	9.575(2)	12.352(1)
c [Å]	20.582 (4)	21.509(4)	12.777(1)
α [°]	90	90	75.940(1)
β [°]	90	109.750(10)	80.660(1)
γ [°]	90	90	79.920(1)
Volume [Å^3]	6113(2)	2891.0(10)	1669.5(2)
Z	8	4	2
Density (calculated)	1.331 Mg/m^3	1.260 Mg/m^3	1.449 Mg/m^3
Absorption coefficient	0.470 mm^{-1}	0.470 mm^{-1}	0.757 mm^{-1}
F(000)	2528	1152	740
Crystal size [mm]	0.38 x 0.2 x 0.2	0.32 x 0.28 x 0.37	0.22 x 0.2 x 0.18
Theta range for data collection [°]	2.51 to 27.05	2.57 to 27.06	2.11 to 27.06
Index ranges	$0 \le h \le 23$, $0 \le k \le 20$, $0 \le l \le 26$	$0 \le h \le 19$, $0 \le k \le 12$, $-27 \le l \le 25$	$0 \le h \le 14$, $-15 \le k \le 15$, $-16 \le l \le 16$
Reflections collected	6687	6586	7711
Independent reflections	6687 [R(int) = 0.0500]	6345 [R(int) = 0.0195]	7329 [R(int) = 0.0308]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6684 / 0 / 379	6341 / 0 / 457	7327 / 0 / 508
Goodness-of-fit on F^2	0.798	1.099	1.098
Final R indices [I>2σ (I)]	$R_1 = 0.0389$, $wR_2 = 0.0749$	$R_1 = 0.0530$, $wR^2 = 0.1046$	$R_1 = 0.0502$, $wR^2 = 0.1028$
R indices (all data)	$R_1 = 0.0980$, $wR_2 = 0.0879$	$R_1 = 0.0795$, $wR^2 = 0.1145$	$R_1 = 0.0724$, $wR^2 = 0.1123$
Largest diff. peak and hole [eÅ^{-3}]	0.182 and - 0.263	0.240 and -0.244	0.353 and -0.253

(40) [ν(C≡O)]; IR (diffuse reflection): 2041.9 (55), 1959.9 (40), 1900.7 (100), 1872.2 (90) [ν(C≡O)]. − MS (70 eV), *m/z* (%): 612 [M$^+$]. − $C_{34}H_{25}CrO_6P$ (612.5): calcd. C 66.67, H 4.11; found C 66.49, H 4.36.

Pentacarbonyl[3-(dimethylphenylphosphonio)-1-ethoxy-3-phenyl-1,2-propadienide]chromium (**5b**): 350 mg (1.00 mmol) of **1a** is added to 138 mg (1.00 mmol) of dimethylphenylphosphane (**4b**) in 3 ml of pentane with vigorous stirring at 20°C in a 5-ml srew-top vessel. Compound **5b** separates as yellowish crystals which are collected by centrifugation; yield: 454 mg (93%), m.p. 97°C. − ^{1}H NMR ($CDCl_3$): δ = 7.77, 7.70, 7.63 (2:1:2 H, m each, PPh); 7.21, 7.10 (4:1 H, m each, 3-Ph); 3.61 (2 H, m, diastereotopic OCH_2), 2.15 and 2.10 [3 H each, d each, ^1J(P,C) = 9.3 and 9.3 Hz, diastereotopic CH_3, PMe_2), 1.33 (3 H, CH_2CH_3). − ^{13}C NMR ($CDCl_3$): δ = 226.4 and 220.8 [1:4, *trans*- and *cis*-CO, $(CO)_5Cr$], 190.5 [C(q), d, ^3J(P,C) = 13.1 Hz, C1], 158.0 [C(q), d, ^2J(P,C) = 13.1 Hz, C2], 135.5 [C(q), d, ^2J(P,C) = 17.5 Hz, 3-Ph], 134.3 (CH, C4', PPh), 131.0 [CH, d, ^3J(P,C) = 8.7 Hz, PPh], 130.3 [CH, d, ^2J(P,C) = 13.2 Hz, PPh]; 129.0, 126.5, 126.4 (CH each, 2:2:1, 3-Ph); 124.3 [C(q), d, ^1J(P,C) = 78.8 Hz, C1', PPh], 75.0 [C(q), d, ^1J(P,C) = 96.0 Hz, C3], 71.3 (OCH_2); 15.6 (CH_3, OEt), 13.0 [CH_3, ^1J(P,C) = 65.3 Hz, PMe], 12.0 [CH_3, ^1J(P,C) = 56.7 Hz, PMe]. − IR (hexane), (%): $\tilde{\nu}$ = 2044.4 cm^{-1} (20), 1963.0 (10), 1912.4 (100), 1878.4 (40) [ν(C≡O)]; IR (diffuse reflection): 2042.6 (50), 1962.6 (30), 1904.7 (100), 1880.4 (60) [ν(C≡O)]. − MS (70 eV), *m/z* (%): 488 (5) [M$^+$], 460 (20), 432 (1), 404 (40), 388 (100) [M$^+$ − CO]. − $C_{24}H_{21}CrO_6P$ (488.4): calcd. C 59.02, H 4.33; found C 58.82, H 4.55.

Pentacarbonyl[1-ethoxy-4,4-dimethyl-3-(triphenylphosphonio)-1,2-pentadienide]chromium (**5c**): 330 mg (1.00 mmol) of pentacarbonyl(1-ethoxy-4,4-dimethyl-2-pentynylidene)chromium (**1b**) is added to 262 mg (1.00 mmol) of triphenylphosphane (**4a**) in 3 ml of pentane with vigorous stirring at 20°C in a centrifuge tube. Compound **5c** separates in yellowish crystals which are collected and washed twice with 3 ml of pentane each; yield: 556 mg (94%), m.p. 102°C. − ^{1}H NMR (CD_3COCD_3, −30°C): δ = 7.9−7.4 (15 H, m, PPh_3), 3.51 and 3.35 (1:1 H, m each, diastereotopic OCH_2), 1.30 (3 H, CH_2CH_3), 1.05 (9 H, s, *t*Bu). − ^{13}C NMR ($CDCl_3$): δ = 226.0 and 220.9 [1:4, *trans*- and *cis*-CO, $(CO)_5Cr$], 204.2 [C(q), d, ^3J(P,C) = 12.6 Hz, C1], 159.6 [C(q), d, ^2J(P,C) = 13.7 Hz, C2], 135.3 [C(q), d, ^2J(P,C) = 9 Hz, 3-Ph], 134.4 (CH, C4', PPh), 130.1 [CH, d, ^3J(P,C) = 11 Hz, PPh_3], 130.3 [CH, d, ^2J(P,C) = 13.2 Hz, PPh_3], 123.5 [C(q), d, ^1J(P,C) = 81 Hz, C1', PPh_3], 83.8 [C(q), d, ^1J(P,C) = 76.0 Hz, C3], 69.8 (OCH_2), 37.4 [C(q), ^2J(P,C) = 19 Hz, CMe_3], 31.5 (3 CH_3, *t*Bu), 15.6 (CH_3, OEt). − IR (diffuse reflection), (%): $\tilde{\nu}$ = 2040.5 cm^{-1} (55), 1952.0 (40), 1900.1 (100), 1869.4 (80) [ν(C≡O)]. − $C_{32}H_{29}CrO_6P$ (592.6): calcd. C 64.86, H 4.93; found C 65.00, H 5.07.

Pentacarbonyl[1-ethoxy-3-phenyl-3-(triphenylphosphonio)-1,2-propadienide]tungsten (**5d**): 482 mg (1.00 mmol) of pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1c**) is added to 262 mg (1.00 mmol) of triphenylphosphane (**4a**) in 3 ml of pentane with vigorous stirring at 20°C in a centrifuge tube. Compound **5d** separates as yellowish crystals which are washed twice with 3 ml of pentane each; yield: 720 mg (97%), m.p. 119°C. − ^{1}H NMR (C_6D_6): δ = 7.46, 7.05, 6.95 (6:3:6 H, m each, PPh); 7.05, 7.00, 6.85 (2:2:1 H, m each, 3-Ph), 3.60 and 3.25 (1 H each, m each, diastereotopic OCH_2), 1.25 (3 H, CH_2CH_3). − ^{13}C NMR ($CDCl_3$): δ = 206.0 and 200.8 [1:4, *trans*- and *cis*-CO, $(CO)_5W$], 204.0 [C(q), d, ^3J(P,C) = 13.0 Hz, C1], 150.0 [C(q), d, ^2J(P,C) = 13.1 Hz, C2], 136.5 [C(q), d, ^{2}J(P,C) = 21.8 Hz, 3-Ph], 134.8 (CH, C4′, PPh), 134.3 [CH, d, ^{3}J(P,C) = 8.7 Hz, PPh], 129.9 [CH, d, ^{2}J(P,C) = 13.1 Hz, PPh]; 128.4, 127.3, 125.8 (CH each, 2:2:1, 3-Ph); 123.3 [C(q), d, ^{1}J(P,C) = 87.2 Hz, C1′, PPh], 75.6 [C(q), d, ^{1}J(P,C) = 96.0 Hz, C3], 70.3 (OCH$_2$); 15.5 (CH$_3$, OEt). – IR (hexane), (%): $\tilde{\nu}$ = 2054.2 cm^{-1} (20), 1976.4 (30), 1911.2 (100), 1873.0 (40) [ν(C≡O)]; IR (diffuse reflection): 2051.8 (50), 1959.5 (40), 1899.5 (100), 1866.0 (90) [ν(C≡O)]. – $C_{34}H_{25}O_6PW$ (744.4): calcd. C 54.86, H 3.39; found C 54.66, H 3.48.

Pentacarbonyl[3-(dimethylphenylphosphonio)-1-ethoxy-3-phenyl-1,2-propadienide]tungsten (**5e**): 482 mg (1.00 mmol) of **1c** is added to 135 mg (1.00 mmol) of dimethylphenylphosphane (**4b**) in 3 ml of pentane with vigorous stirring at 20°C in a 5-ml srew-top vessel. Compound **5e** separates as yellowish crystals which are collected by centrifugation; yield: 582 mg (94%), m.p. 91°C. – ^{1}H NMR (CDCl$_3$): δ = 7.28, 7.15, 7.06, 6.91 (4:1:4:1 H, m each, 2 Ph); 3.61 (2 H, m, diastereotopic OCH$_2$), 1.47 and 1.41 [3 H each, d each, ^{1}J(P,C) = 8.5 Hz each, diastereotopic CH$_3$, PMe$_2$], 1.22 (3 H, CH$_2$C*H*$_3$). – ^{13}C NMR (CDCl$_3$): δ = 206.4 and 201.9 [1:4, *trans*- and *cis*-CO, (CO)$_5$W], 198.7 [C(q), d, ^{3}J(P,C) = 13.0 Hz, C1], 148.1 [C(q), d, ^{2}J(P,C) = 13.1 Hz, C2], 135.5 [C(q), d, ^{2}J(P,C) = 17.4 Hz, 3-Ph], 134.0 (CH, C4′, PPh), 131.1 [CH, d, ^{3}J(P,C) = 8.8 Hz, PPh], 130.3 [CH, d, ^{2}J(P,C) = 13.0 Hz, PPh]; 129.3, 127.0, 126.0 (CH each, 2:1:2, 3-Ph); 124.5 [C(q), d, ^{1}J(P,C) = 78.5 Hz, C1′, PPh], 76.0 [C(q), d, ^{1}J(P,C) = 96.0 Hz, C3], 71.0 (OCH$_2$); 15.7 (CH$_3$, OEt), 12.2 [CH$_3$, ^{1}J(P,C) = 65.4 Hz, PMe], 10.0 [CH$_3$, ^{1}J(P,C) = 56.7 Hz, PMe]. – IR (hexane), (%): $\tilde{\nu}$ = 2055.9 cm^{-1} (20), 1975.2 (30), 1917.0 (100), 1845.0 (40) [ν(C≡O)]; IR (diffuse reflection): 2054.8 (10), 1973.6 (40), 1913.2 (100), 1849.7 (60) [ν(C≡O)]. – MS (70 eV), *m/z* (%): 620 (5) [M$^+$], 592 (20) [M$^+$ – CO] (10), 564 (5), 536 (10), 480 [M$^+$ – 5 CO], 138 (100) [PhMe$_2$P$^+$], 123 (95) [138 – Me]. – $C_{24}H_{21}O_6PW$ (620.3): calcd. C 46.48, H 3.41; found C 46.34, H 3.54.

Pentacarbonyl[1-ethoxy-3-(trimethylsilyl)-3-(triphenylphosphonio)-1,2-propadienide]tungsten (**5f**): 478 mg (1.00 mmol) of pentacarbonyl[1-ethoxy-3-(trimethylsilyl)-2-propynylidene]tung sten (**1d**) is added to 262 mg (1.00 mmol) of triphenylphosphane (**4a**) in 3 ml of dry pentane with vigorous stirring at 20°C in a 5-ml srew-top vessel. Compound **5f** separates as white crystals, which are collected by centrifugation and washed three times with hexane; yield: 666 mg (90%). – ^{1}H NMR (CDCl$_3$): δ = 7.70, 7.60, 7.15 (3:11:6 H, m each, 4 Ph); 3.50 and 3.05 (1 H each, m each, diastereotopic OCH$_2$), 1.15 (3 H, CH$_2$C*H*$_3$). – ^{13}C NMR (CDCl$_3$): δ = 212.7 [C(q), d, ^{3}J(P,C) = 13.0 Hz, C1], 205.8 and 200.3 [1:4, *trans*- and *cis*-CO, (CO)$_5$W], 139.6 [C(q), d, ^{2}J(P,C) = 17.4 Hz, C2], 133.3 (CH, C4′, PPh), 133.8 [CH, d, ^{3}J(P,C) = 8.7 Hz, PPh], 128.9 [CH, d, ^{2}J(P,C) = 13.1 Hz, PPh], 122.4 [C(q), d, ^{1}J(P,C) = 87.3 Hz, C1′, PPh], 69.3 (OCH$_2$), 65.3 [C(q), d, ^{1}J(P,C) = 47.9 Hz, C3], 15.0 (CH$_3$, OEt), 0.1 (3 CH$_3$, SiMe$_3$). – IR (diffuse reflection), (%): $\tilde{\nu}$ = 2052.2 cm^{-1} (40), 1957.1 (30), 1917.3 (100), 1869.9 (90) [ν(C≡O)]. – MS-FD, *m/z* (%), ^{184}W: 741 [M$^+$]. – $C_{31}H_{29}O_6PSiW$ (740.5): calcd. C 50.28, H 3.95; found C 50.49, H 4.08.

[3-(Di-tert-butylphosphanyl)-1-ethoxy-3-phenylpropenylidene]pentacarbonylchromium [(*E*)-**8g**] *and Decacarbonyl-μ-[3-(di-tert-butylphosphanyl)-1-ethoxy-3-phenylpropenylidene-C1,P]-dichromium* [(*E*)-**9g**]: 350 mg (1.00 mmol) of **1a** is added to 146 mg (1.00 mmol) of di-*tert*-butylphosphane (**6a**) in 3 ml of pentane with vigorous stirring at 20°C in a 5-ml srew-top vessel. Immediate precipitation of a red solid occurs. The mixture is treated with ultrasound for homogenization, and dark red crystals of (*E*)-**8g** are collected by centrifugation; yield: 400 mg (81%), R_f = 0.3 (in dichloromethane/pentane, 1:6), m.p. 84°C. Chromatography of the mother liquor on silica gel affords further 40 mg of (*E*)-**8g**. R_f = 0.40 (in pentane/dichloromethane, 10:1) as well as the red dinuclear complex (*E*)-**9g**, R_f = 0.45 (in pentane/dichloromethane, 10:1), 34 mg (5%), red crystals from pentane, m.p. 116°C.

(*E*)-**8g**: ^{1}H NMR (C$_6$D$_6$): δ = 7.85 (1 H, s, 2-H); 7.30, 6.96, 6.88 (2:2:1 H, m each, 3-Ph); 4.25 (2 H, q, OCH$_2$), 1.20 and 1.15 (9 H each, diastereotopic *t*Bu$_2$P), 0.40 (3 H, t, CH$_2$C*H*$_3$). – ^{13}C NMR (C$_6$D$_6$): δ = 339.0 (Cr=C), 224.5 and 217.5 [1:4, *trans*- and *cis*-CO, (CO)$_5$Cr], 149.3 (CH, ^{3}J = 3 Hz, C2), 145.2 [C(q), d, ^{1}J(P,C) = 24 Hz, *i*C, Ph], 143.6 [C(q), d, ^{1}J(P,C) = 45 Hz, C3]; 131.2, 130.4, 126.9 (2:2:1, CH each, Ph); 76.8 (OCH$_2$); 34.2 and 33.8 (C(q) each, *C*Me$_3$); 31.7 and 31.1 (CH$_3$ each, two diastereotopic *t*Bu), 13.9 (CH$_2$*C*H$_3$). – IR (hexane), (%): $\tilde{\nu}$ = 2056.4 cm^{-1} (20), 1985.6 (5), 1944.7 (100) [ν(C≡O)]. – MS (70 eV), *m/z* (%): 496 (20) [M$^+$], 468 (2), 440 (10), 412 (20), 384 (20), 356 (40) [M$^+$ – CO], 199 (40), 171 (40), 131 (50), 57 (100). – $C_{24}H_{28}CrO_6P$ (495.5): calcd. C 58.18, H 5.70; found C 57.98; H 5.94.

(*E*)-**9g**: ^{1}H NMR (C$_6$D$_6$): δ = 8.05 [1 H, d, ^{3}J(P,H) = 14.0 Hz, 2-H], 7.20 and 6.95 (2:3 H, m each, Ph), 4.20 (2 H, q, OCH$_2$), 1.25 [18 H, d dynamically broadened, ^{3}J(P,H) = 14 Hz, averaged signal of the diastereotopic *t*Bu groups], 0.70 (3 H, t, CH$_3$, Et). – IR (hexane), (%): $\tilde{\nu}$ = 2057.6 cm^{-1} (20), 1983.0 (5), 1946.6 (100) [ν(C≡O)] of (CO)$_5$Cr=C; 2064.8 (30), 1930.3 (70) [ν(C≡O)] of (CO)$_5$CrP. – $C_{29}H_{28}Cr_2O_{11}P$ (687.5): calcd. C 50.66, H 4.11; found C 50.83, H 4.22.

Pentacarbonyl[3-(dicyclohexylphosphanyl)-1-ethoxy-3-phenylpropenylidene]chromium [(*E*)-**8h**] *and Decacarbonyl-μ-[3-(dicyclohexylphosphanyl)-1-ethoxy-3-phenylpropenylidene-C1,P]-dichromium* [(*E*)-**9h**]: 350 mg (1.00 mmol) of **1a** is added to 198 mg (1.00 mmol) of dicyclohexylphosphane (**6b**) in 3 ml of pentane with vigorous stirring at 20°C in a 5-ml srew-top vessel. Chromatography of the red solution (silica gel, column 20 × 2 cm, dichloromethane/pentane, 1:10) yields two red compounds of similar R_f values, (*E*)-**9h** [55 mg (7%), R_f = 0.45 (in dichloromethane/pentane, 1:10), dark-red crystals from pentane at –15°C, m.p. 124°C] and (*E*)-**8h** [422 mg (77%), R_f = 0.40 (in dichloromethane/pentane, 1:10), red crystals from pentane, m.p. 84°C].

(*E*)-**8h**: ^{1}H NMR (C$_6$D$_6$): δ = 7.60 (1 H, s, 2-H); 7.25, 7.00, 6.95 (2:2:1 H, m each, 3-Ph); 4.35 (2 H, q, OCH$_2$), 1.98–0.80 (22 H, 2 Cy$_2$P), 0.45 (3 H, t, CH$_2$C*H*$_3$). – ^{13}C NMR (C$_6$D$_6$): δ = 336.7 (Cr=C), 224.5 and 217.6 [1:4, *trans*- and *cis*-CO, (CO)$_5$Cr], 146.1 (CH, ^{3}J = 6 Hz, C2), 143.8 [C(q), d, ^{1}J(P,C) = 37 Hz, C3], 143.1 [C(q), d, ^{1}J(P,C) = 17 Hz, *i*C, Ph]; 129.4, 128.8, 126.4 (2:2:1, CH each, Ph); 76.8 (OCH$_2$); 33.9 [CH, d, ^{1}J(P,C) = 17.5 Hz, C1′], 31.0 and 29.8 [CH$_2$ each, d each, ^{2}J(P,C) = 8.7 Hz, C2′,6′], 27.8 and 27.3 [CH$_2$ each, d each, ^{2}J(P,C) = 8.5 Hz, C3′,5′], 26.7 (CH$_2$, C4′), 13.6 (CH$_2$*C*H$_3$). – MS (70 eV), *m/z* (%): 548 (40) [M$^+$], 520 (10), 492 (20), 464 (30), 408 (100) [M$^+$ – 5 CO]. – IR (hexane), (%): $\tilde{\nu}$ = 2055.9 cm^{-1} (25), 1983.3 (5), 1942.9 (100) [ν(C≡O)]; (diffuse reflection): 2054.9 (60), 1978.8 (20), 1925.9 (100) [ν(C≡O)]; 1522.6 [ν(C=C)]. – $C_{28}H_{33}CrO_6P$ (548.5): calcd. C 61.31, H 6.06; found C 61.51, H 6.29.

(*E*)-**9h**: ^{1}H NMR (C$_6$D$_6$): δ = 8.10 [1 H, d, ^{3}J(P,H) = 15.2 Hz, 3-H]; 7.03, 6.95, 6.80 (2:2:1 H, m each, 3-Ph); 4.30 (2 H, m, diastereotopic OCH$_2$); 2.15, 2.00, 1.72, 1.50, 1.30, 1.10, 0.90 (2:2:4:4:3:4:3 H, m each, 2 diastereotopic *c*C$_6$H$_{11}$); 0.50 (3 H, t, CH$_2$C*H*$_3$). – ^{13}C NMR (CDCl$_3$): δ = 341.3 (Cr=C), 223.9 and 216.5 [1:4, *trans*- and *cis*-CO, 1-(CO)$_5$Cr], 221.5 and 218.6 [1:4, ^{2}J(P,C) = 6 and 13 Hz, *trans*- and *cis*-CO, P(CO)$_5$Cr], 154.9 [CH, d, ^{2}J(P,C) = 13 Hz, C2], 138.8 [C(q), *i*C, 4-Ph], 134.5 [C(q), ^{1}J(P,C) = 11 Hz, C3]; 129.3, 128.2, 127.9 (CH each, 2:2:1, 3-Ph), 77.6 (OCH$_2$), 38.8 [2 CH, ^{1}J(P,C) = 17.4 Hz, 2 *c*C$_6$H$_{11}$], 27.8 and 27.6 [2 CH$_2$ each, ^{2}J(P,C) = 8.6 Hz each, *c*C$_6$H$_{11}$], 28.8 and 26.4

[4:2, CH$_2$ each, C3',4', cC$_6$H$_{11}$], 14.0 (CH$_3$, OEt). – IR (hexane), (%): $\tilde{\nu}$ = 2063.5 cm^{-1} (30), 2057.8 (20), 1983.3 (5), 1947.9 (100), 1929.1 (80) [ν(C≡O)]. – MS-FD, *m/z*: 741 [M$^+$]. – MS (70 eV), *m/z* (%): 740 (20) [M$^+$], 656 (20), 600 (10) [M$^+$ – 5 CO], 548 (15) [600 – Cr], 408 (50) [600 – Cr(CO)$_5$], 365 (30), 328 (30), 220 (50) [Cr(CO)$_6$], 108 (100). – $C_{33}H_{33}Cr_2O_{11}P$ (740.6): calcd. C 53.52, H 4.49; found C 53.62, H 4.70.

Pentacarbonyl[3-(diphenylphosphanyl)-1-ethoxy-3-phenylpropenylidene]chromium [(*E*)-**8i**] *and Decacarbonyl-μ-[3-(diphenylphosphanyl)-1-ethoxy-3-phenylpropenylidene-C1,P]-dichromium* [(*E*)-(**9i**)]: 350 mg (1.00 mmol) of **1a** is added to 186 mg (1.00 mmol) of diphenylphosphane (**6c**) in 3 ml of pentane with vigorous stirring at 20°C in a 5-ml srew-top vessel. Chromatography of the red solution (silica gel, column 20 × 2 cm, dichloromethane/pentane, 1:10) yields two red compounds of similar R_f values, (*E*)-(**9i**) [64 mg (9%), R_f = 0.45 (in dichloromethane/pentane, 1:10), dark-red crystals from pentane at –15°C, m.p. 118°C] and (*E*)-**8i** [180 mg (34%), R_f = 0.4 (in dichloromethane/pentane, 1:10), m.p. 93°C].

[(*E*)-**8i**]: ^{1}H NMR (C$_6$D$_6$): δ = 7.58, 7.53, 7.10–7.00 (2:2:6H, m each, diastereotopic PPh$_2$); 7.35, 6.95, 6.85 (2:2:1 H, m each, 3-Ph); 4.28 (2H, q, OCH$_2$), 0.50 (3H, t, CH$_2$C*H*$_3$). – ^{13}C NMR (C$_6$D$_6$): δ = 338.6 (Cr=C), 223.9 and 216.4 [1:4, *trans*- and *cis*-CO, (CO)$_5$Cr], 147.0 [CH, ^3J(P,C) = 9 Hz, C2], 141.8 [C(q), d, ^1J(P,C) = 39 Hz, C3], 140.0 [C(q), d, ^1J(P,C) = 26 Hz, *i*C, Ph], 136.8 and 136.3 [C(q) each, ^1J(P,C) = 12 and 14 Hz, resp.; diastereotopic *i*C PPh each); 135.5, 133.8, 130.4, 129.4, 128.9, 128.6 (2:2:2:2:1:1, CH each, diastereotopic PPh$_2$]; 129.6, 128.8, 127.9 (2:2:1, CH each, 3-Ph); 76.2 (OCH$_2$), 13.3 (CH$_2$*C*H$_3$). – IR (hexane), (%): $\tilde{\nu}$ = 2059.5 cm^{-1} (25), 1987.9 (5), 1945.3 (100) [ν(C≡O)]. – $C_{28}H_{21}CrO_6P$ (536.4): calcd. C 62.69, H 3.95; found C 62.75, H 4.00.

(*E*)-**9i**: ^{1}H NMR (C$_6$D$_6$): δ = 7.93 [1H, d, ^3J(P,H) = 15.5 Hz, 2-H]; 7.65 and 7.61 (2:2, m each, *o*H, PPh), 7.03 (8H, *m*- and *p*H of PPh, and *o*H of 3-Ph), 6.78 and 6.68 (2:1H, m each, *m*- and *p*H of 3-Ph), 4.20 (2H, m, diastereotopic OCH$_2$), 0.45 (3H, t, CH$_2$C*H*$_3$). – ^{13}C NMR (CDCl$_3$): δ = 343.5 (Cr=C), 223.8 and 216.2 [1:4, *trans*- and *cis*-CO, 1-(CO)$_5$Cr], 221.4 and 216.8 [1:4, ^2J(P,C) = 6.5 and 15 Hz, *trans*- and *cis*-CO, P(CO)$_5$Cr], 150.6 [CH, d, ^2J(P,C) = 10.9 Hz, C2], 134.0 (C(q), ^1J(P,C) = 27 Hz, C3), 137.4 [C(q), *i*C 3-Ph], 128.8 [C(q), 2 *i*C, PPh]; 133.4 [4 CH, ^2J(P,C) = 10.9 Hz, *o*C, PPh], 130.8 (2 CH, *p*C, PPh), 128.9 [4 CH, ^3J(P,C) = 8.5 Hz, *m*C, PPh]; 130.0, 128.8, 128.5 (2:2:1, CH each, 3-Ph); 77.4 (OCH$_2$), 14.1 (CH$_3$, OEt). – IR (hexane), (%): $\tilde{\nu}$ = 2065.6 cm^{-1} (20), 2059.9 (25), 1984.3 (5), 1952.8 (100), 1936.5 (80) [ν(C≡O)]. – $C_{33}H_{21}Cr_2O_{11}P$ (728.5): calcd. C 54.41, H 2.91; found C 54.40, H 3.08.

Pentacarbonyl[3-(di-tert-butylphosphanyl)-1-ethoxy-3-phenylpropenylidene)tungsten [(*E*)-**8k**] *and Decacarbonyl-μ-[3-(di-tert-butylphosphanyl)-1-ethoxy-3-phenylpropenylidene-C1,P]-ditungsten* [(*E*)-**9k**]: 482 mg (1.00 mmol) of **1c** is added to 146 mg (1.00 mmol) of di-*tert*-butylphosphane (**6a**) in 3 ml of dry pentane with vigorous stirring at 20°C in a 5-ml srew-top vessel. (*E*)-**8k** separates at –78°C in dark red crystals [501 mg (80%), m.p. 79°C]. Chromatography of the mother liquor yields 60 mg of (*E*)-**8k** (R_f = 0.40 in dichloromethane/pentane, 1:10) and (*E*)-**9k** (R_f = 0.45 in pentane/dichloromethane, 1:10), dark red crystals from pentane [50 mg (5%), m.p. 119°C].

(*E*)-**8k**: ^{1}H NMR (C$_6$D$_6$): δ = 7.78 (1H, s, 2-H); 7.30, 6.96, 6.89 (2:2:1H, m each, 3-Ph); 4.15 (2H, q, OCH$_2$), 1.22 and 1.16 (9H each, diastereotopic *t*Bu$_2$P), 0.45 (3H, t, CH$_2$C*H*$_3$). – ^{13}C NMR (C$_6$D$_6$): δ = 311.7 (W=C), 204.1 and 198.3 [1:4, *trans*- and *cis*-CO, (CO)$_5$W], 153.0 (CH, ^3J = 3 Hz, C2), 146.4 [C(q), d, ^1J(P,C) = 43 Hz, C3], 145.8 [C(q), d, ^1J(P,C) = 26 Hz, *i*C, Ph]; 130.4, 128.0, 127.0 (2:2:1, CH each, Ph); 79.3 (OCH$_2$); 34.1 and 33.8 [C(q) each, *C*Me$_3$]; 31.7 and 31.0 (CH$_3$ each, two diastereotopic *t*Bu), 13.7 (CH$_2$*C*H$_3$). – IR (hexane), (%): $\tilde{\nu}$ = 2064.5 cm^{-1} (40), 1982.3 (5), 1942.6 (100) [ν(C≡O)]. – MS (70 eV), *m/z* (%), ^{184}W: 627 (10) [M$^+$], 599 (20), 571 (20), 543 (30), 515 85), 487 (30) [M$^+$ – CO], 275 (40), 131 (40), 57 (100). – $C_{24}H_{28}O_6PW$ (627.3): calcd. C 45.95, H 4.50; found C 46.30, H 4.79.

(*E*)-**9k**: ^{1}H NMR (C$_6$D$_6$): δ = 7.85 [1H, d, ^3J(P,H) = 13.5 Hz, 2-H]; 7.35 and 7.00 (2:3, m each, Ph), 4.05 (2H, q, OCH$_2$), 1.30 and 1.05 [9H each, d each, ^3J(P,H) = 14 Hz each, diastereotopic *t*Bu], 0.65 (3H, t, CH$_2$C*H*$_3$). – ^{13}C NMR (C$_6$D$_6$): δ = 316.0 [W=C, ^3J(P,C) = 6 Hz], 202.8 and 198.3 [1:4, ^2J(P,C) = 14 and 7 Hz, *trans*- and *cis*-CO, 1-W(CO)$_5$], 199.3 and 196.9 [1:4, ^3J(P,C) = 7 Hz, *trans*- and *cis*-CO, PW(CO)$_5$], 160.2 [CH, d, ^2J(P,C) = 12 Hz, C2], 138.7 [C(q), ^1J(P,C) = 25 Hz, C3], 137.0 [C(q), *i*C 3-Ph]; 128.8, 128.3 and 127.8 (1:2:2, CH each, Ph); 79.9 (OCH$_2$), 32.4 and 29.9 [C(q) each, ^1J(P,C) = 28 Hz each, diastereotopic *C*Me$_3$], 31.8 and 29.8 (CH$_3$ each, diastereotopic *t*Bu), 14.6 (CH$_3$, OEt). – IR (hexane), (%): $\tilde{\nu}$ = 2068.2 cm^{-1} (20, broad), 1982.3 (5), 1937.8 (100 broad) [ν(C≡O)]. – $C_{29}H_{28}O_{11}PW_2$ (951.2): calcd. C 36.62, H 2.97; found C 36.60, H 3.01.

Pentacarbonyl[3-(dicyclohexylphosphanyl)-1-ethoxy-3-phenylpropenylidene]tungsten [(*E*)-**8l**]: 482 mg (1.00 mmol) of **1c** is added to 198 mg (1.00 mmol) of dicyclohexylphosphane (**4b**) in 3 ml of dry pentane with vigorous stirring at 20°C in a 5-ml srew-top vessel. Compound (*E*)-**8l** remains in the mother liquor and is isolated in dark-red crystals on cooling to –15°C [450 mg (67%), R_f = 0.4 (in dichloromethane/pentane, 1:10), m.p. 93°C]. – ^{1}H NMR (C$_6$D$_6$): δ = 7.55 (1H, s, 2-H); 7.25, 6.95, 6.80 (2:2:1H, m each, 3-Ph); 4.20 (2H, q, OCH$_2$), 2.00–1.00 (22H, 2 Cy$_2$P), 0.50 (3H, t, CH$_2$C*H*$_3$). – ^{13}C NMR (CDCl$_3$): δ = 309.3 (W=C), 204.1 and 198.2 [1:4, *trans*- and *cis*-CO, (CO)$_5$W], 149.5 (CH, ^3J = 5 Hz, C2), 147.2 [C(q), d, ^1J(P,C) = 39 Hz, C3], 143.2 [C(q), d, ^1J(P,C) = 17 Hz, *i*C, Ph]; 129.1, 128.4, 127.8 (2:2:1, CH each, Ph); 79.1 (OCH$_2$); 33.9 [CH, d, ^1J(P,C) = 17.5 Hz, C1'], 31.0 and 29.8 [CH$_2$ each, d each, ^2J(P,C) = 8.7 Hz, C2',6'], 27.8 and 27.3 [CH$_2$ each, d each, ^2J(P,C) = 8.5 Hz, C3',5'], 26.7 (CH$_2$, C4'), 13.6 (CH$_2$*C*H$_3$). – IR (hexane), (%): $\tilde{\nu}$ = 2064.3 cm^{-1} (25), 1974.1 (5), 1941.4 (100) [ν(C≡O)]; (diffuse reflection): 2065.0 (60), 2009.7 (10), 1975.5 (60), 1917.7 (100) [ν(C≡O)]; 1523.6 [ν(C=C)]. – MS-FD, *m/z*: 670 [M$^+$]. – $C_{28}H_{33}O_6PW$ (670.3): calcd. C 50.17, H 3.46; found C 49.93, H 3.50.

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