Organic Syntheses via Transition Metal Complexes. 75.[1] Phosphinonaphthalenes and Phosphinoindenes by Cyclization of Alkynyl Carbene Complexes (M = Cr, W)

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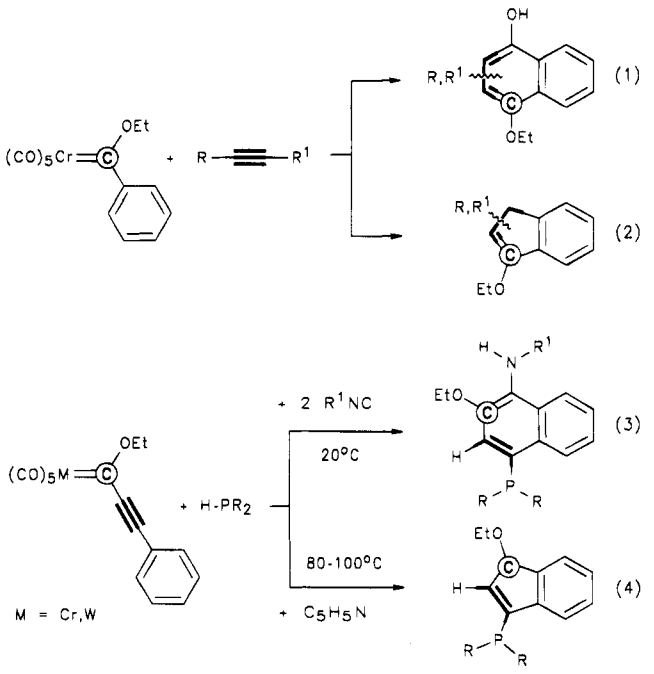
1-Amino-2-ethoxy-4-phosphinonaphthalenes **6a,b** (>90% yields) are obtained from (phenylalkynyl)carbene complexes $(CO)_5M{=}C(OEt){-}C{\equiv}C{-}Ph$ (M = Cr, W) **1** by a novel two-step carbene/alkyne benzannulation. The first step involves the formation of (*E*)-(2-phenyl-2-phosphinoethenyl)carbene complexes $(CO)_5M{=}C(OEt){-}CH{=}C(Ph){-}PR_2$ (*E*)-**3a–c** by 3-addition of secondary phosphines HPR_2 (R = *t*-Bu, *c*-C_6H_{11}) **2a,b** to **1**. A subsequent addition of isocyanides R^1NC (R = *t*-Bu, *c*-C_6H_{11}) **4a,b** to (*E*)-**3a–c** yields ketene imine complexes $(CO)_5M[R^1N{=}C{=}C(OEt){-}CH{=}C(Ph){-}PR_2]$ **A** by the insertion of **4** into the M=C bond of **3**. (Metal-free) ketene imines are generated from **A** by ligand displacement with **4** and cyclize spontaneously to **6**. Thermolysis of (*E*)-**3a–c** affords $(CO)_5M$ phosphinoindene complexes **9** and **10**. Reaction of **9** or **10** with pyridine yields phosphinoindenes **12** and pyridine complexes $(CO)_5M(C_5H_5N)$ **11**. **10a**, $C_{24}H_{29}CrO_6P$, was characterized by X-ray diffraction. It crystallizes in space group $P\bar{1}$ No. 2 with cell parameters a = 9.412(1) Å, b = 11.455(2) Å, c = 11.962(2) Å, = 89.10(1)°, β = 79.09(1)°, γ = 88.60(1)°, Z = 2, R_1 = 0.063, and wR^2 = 0.117.

Benzannulation reactions of (arylcarbene)chromium complexes with alkynes have gained wide application in synthetic organic chemistry.[2] The so-called Dötz reaction involves the insertion of a C≡C into a Cr=C bond and leads to the formation of 1,4-dioxynaphthalenes (Scheme 1, eq 1). Indenes may be obtained as side products (Scheme 1, eq 2).[2,3] Intramolecular Dötz-type cyclizations of (alkynylcarbene)chromium complexes are governed by sterical restrictions.[4] Reactions of this type are achieved only when the reacting groups are tethered properly.[5] We report here on a carbene/alkyne benzannulation, which is different from the Dötz-type reaction. It requires two steps: a Michael addition of a protic nucleophile to a (2-arylalkynyl)carbene complex $(CO)_5M{=}C(OEt){-}C{\equiv}C{-}Ar$ (M = Cr, W) and the cyclization of the Michael adduct by the addition of an isocyanide. First examples of this reaction comprise the formation of 1,4-diamino-2-ethoxynaphthalenes by subsequent addition of a secondary amine and an isocyanide to a (phenylalkynyl)carbene complex $(CO)_5M{=}C(OEt){-}C{\equiv}C{-}Ph$ (M = Cr, W).[6] This novel type carbene/alkyne benzannulation is complementary to the Dötz reaction with regard to its regiochemistry, and insofar as heterosubstituents

Scheme 1. Benzannulation and Formation of Indenes *via* the Arylcarbene/Alkyne (Dötz Reaction) *vs* the (1-Arylalkynyl)carbene Complex Route



[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1994.

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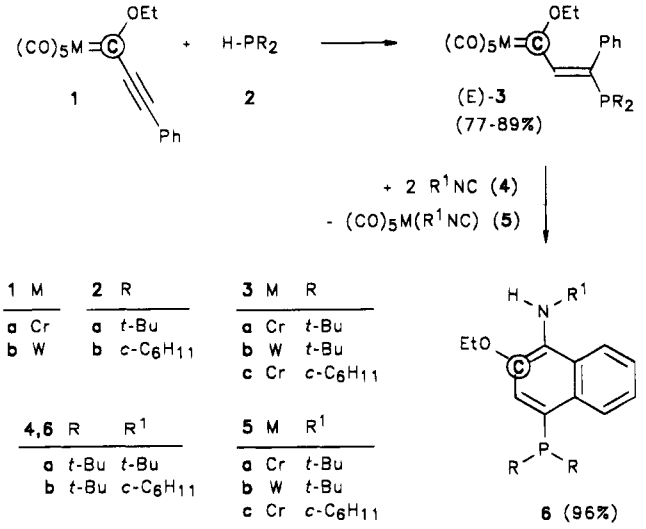
Scheme 2. 1-Amino-4-phosphinonaphthalenes from (Arylalkynyl)carbene Complexes



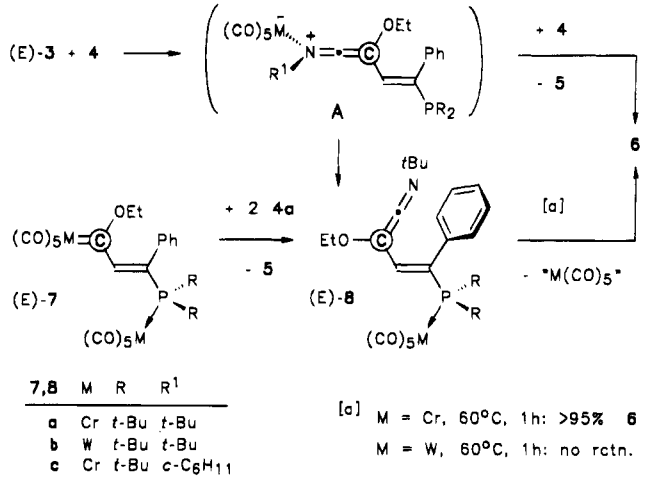
other than those based on oxygen are introduced at 1- and 4-positions of the six-membered ring.

We have extended our studies to the formation of 1-amino-2-ethoxy-4-phosphinonaphthalenes by the stepwise addition of secondary phosphines and isocyanides to (arylalkynyl)carbene complexes (Scheme 1, eq 3). We also report on the generation of phosphinoindenes from such compounds (Scheme 1, eq 4).

Phosphinonaphthalenes 6. The first step of the cyclization of an (arylalkynyl)carbene complex $(CO)_5M$=C(OEt)—C≡C—Ph **1** requires the addition of a protic nucleophile NuH to the alkyne unit in a *syn* fashion, by which an arylalkenyl carbene complex $(CO)_5M$=C(OEt)—CH=C(Nu)Ph **3** of (*E*) configuration is generated. The (*E*) configuration is the stereochemical prerequisite for the subsequent cyclization. Thus, the stereochemistry of the 3-addition of NuH to **1** is crucial. Depending on the type of nucleophile involved, its addition to **1** may be highly stereoselective in one or the other direction.[7] The stereodifferentiation apparently results from different protonation sites of the zwitterionic $(CO)_5M^-$-[C(OEt)=C=C(Ph)NuH^+] and anionic allene-type intermediates $(CO)_5M[C(OEt)=C=C(Ph)Nu]^-$,[1] which are formed as the primary adducts of NuH and its conjugate base Nu^-, respectively, to **1**.[7i] For the present case, the addition of a secondary phosphine H-PR_2 **2** to **1** is stereochemically uniform and leads to (2-phosphino-2-arylethenyl)carbene complexes (*E*)-**3a**–**c** of proper (*E*) configuration (Scheme 2) in 77–89% chemical yields (R = *tert*-Bu, *c*-C_6H_{11}).[1] Side reactions comprise the formation of small amounts of binuclear complexes (*E*)-**7** (Scheme 3).[1]

The alkenylcarbene complexes (*E*)-**3a**–**c** react with isocyanides **4a,b** under mild conditions and afford 1-amino-2-ethoxy-4-phosphinonaphthalenes **6a,b** in 96% yields (Scheme 2). The key step of this reaction consists

Scheme 3. Ketene Imine Complexes A and (*E*)-8 as Key Intermediates



in the insertion of an isocyanide **4** into the M=C bond of (*E*)-**3** with formation of a ketene imine complex **A** (Scheme 3).[6,8,9] Subsequently, **A** takes up a further equivalent of **4** and yields an isocyanide complex **5** by displacement of the ketene imine ligand. The latter cyclizes spontaneously at 20 °C to the naphthalene **6**. Ketene imine complexes (*E*)-**8a,c**, which are coordination isomers of **A**, are more stable thermally than **A**, due to steric hindrance of the cyclization step by the bulkiness of the $(CO)_5MP(tert\text{-}Bu)_2$ unit. These compounds are generated by addition of 2 equiv of **4a** to the *binuclear* complexes (*E*)-**7a,c**[1] and could be characterized spectroscopically at 20 °C. The cyclization of (*E*)-**8a,c** to naphthalenes **6** requires heating to 60 °C in order to induce the disengagement of the $(CO)_5M$ moiety from the phosphorus atom. Thus, naphthalenes **6** are obtained from both, compounds **A** and their coordination isomers (*E*)-**8**, though different reaction temperatures are required.

Phosphinoindenes 9, 10, and 12. Indenes are formed on reaction of arylcarbene complexes with alkynes as side products of the Dötz reaction.[2,3] A different approach to the synthesis of indenes from carbene complexes is based on the cyclization of the C_5 skeleton of the (2-aryl-1-alkynyl)carbene ligand of **1**.

Phosphinoindenes **12** are generated together with pyridine complexes $(CO)_5M(C_5H_5N)$ **11** in two steps, by the addition of secondary phosphines **2** to **1**, which leads to the formation of (2-phosphinoethenyl)carbene complexes (*E*)-**3** (Scheme 2) and the thermolysis of (*E*)-**3** in the presence of pyridine at 80–100 °C (Scheme 4; M = Cr, W; > 90% yields). Complexes **11** are removed most conveniently and almost quantitatively from the reaction mixture by crystallization from heptane at −15 °C, under which conditions compounds **12** are accumulated in the mother liquor.

The cyclization of (*E*)-**3** to **12** involves the formation of phosphino complexes **9** and **10** as intermediate products (Scheme 4). Compounds **9** are generated from (*E*)-**3**, supposedly by an attack of the carbene carbon atom at the aromatic ring.[10] A zwitterionic species **B**

(7) (a) Fischer, E. O.; Kreissl, F. R. *J. Organomet. Chem.* **1972**, *35*, C47. (b) Fischer, E. O.; Kalder, H. J. *J. Organomet. Chem.* **1977**, *131*, 57. (c) Duetsch, M.; Stein, F.; Lackmann, R.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Chem. Ber.* **1992**, *125*, 2051. (d) Aumann, R.; Hinterding, P. *Chem. Ber.* **1992**, *125*, 2765. (e) Aumann, R.; Hinterding, P. *Chem. Ber.* **1993**, *126*, 421. (f) Camps, F.; Llebaria, A.; Moretó, J. M.; Ricart, S.; Viñas, S.; Ros, J.; Yánez, R. *J. Organomet. Chem.* **1991**, *401*, C17. (g) Aumann, R.; *Chem. Ber.* **1992**, *125*, 2773. (h) Wang, S. L. B.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 4550. (i) Aumann, R.; Jasper, B.; Läge, M.; Krebs, B. *Organometallics* **1994**, *13*, 3502.

(8) Review on this reaction type: Aumann, R. *Angew. Chem.* **1988**, *100*, 1512–1524; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1456–1467.

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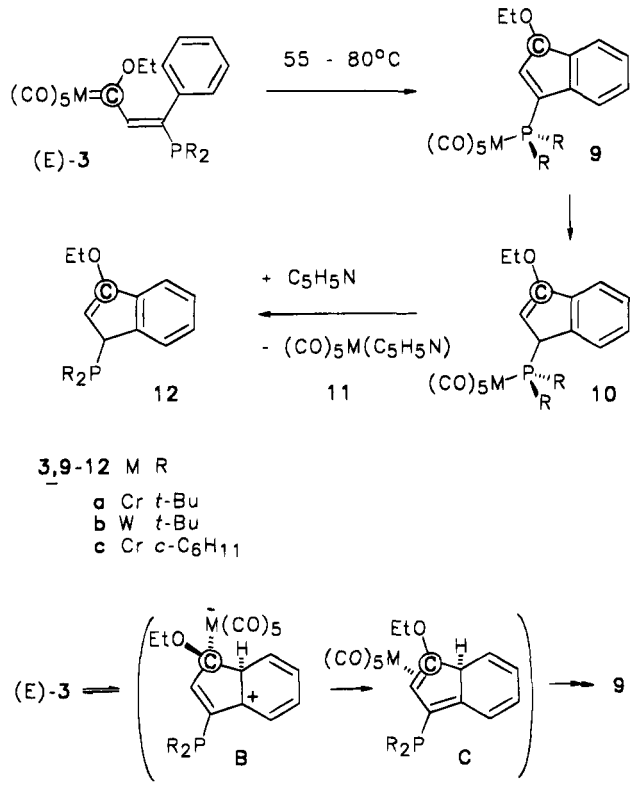
Scheme 4. Cyclization of (2-Phosphinoethenyl)carbene Complexes (*E*)-3 (M = Cr, W) with Formation of Phosphino Indenes 12 *via* 9 and 10



may be formed initially and rearrange fast to an olefin complex **C**. The $(CO)_5M$ moiety of **C** could migrate to the phosphorus atom without losing contact to the indene skeleton. A (suprafacial) 1,5 hydrogen shift of the rearranged product may finally lead to **9**. The chromium complex **9a** can be isolated. It forms an isomer **9'a** in solution at 80 °C, while the tungsten complex **9b** remains unchanged for several hours even at 100 °C. ^{1}H NMR spectra of **9a** and **9'a** may be closely similar to each other with respect to the chemical shifts and the proton coupling pattern except for the vicinal couplings ^3J(P,2-H), which amount to 5.5 and 2.5 Hz, respectively. The different coupling constants may be attributed to the influence of conformational effects, for which Karplus-like curves have been established in the case of phosphine oxides and related compounds.[11]

The product composition resulting from the thermolysis of **3a–c** in the presence of equivalent amounts of pyridine was analyzed by ^{1}H NMR measurements (C_6D_6, 360 MHz) under different reaction conditions (Table 1). In the multi-step rearrangement sequence from (*E*)-**3** to **10**, the $M(CO)_5$ unit is not trapped by pyridine and therefore appears to remain in close contact to the indene ligand. We conclude that the isomerization of the rotamers **9a** and **9a'** might be initiated by a shift of the metal moiety from the phosphorus atom to the C=C bond of the indene skeleton and a rotation/inversion of the (slightly tilted) P*t*-Bu_2 unit. This process may require less energy than

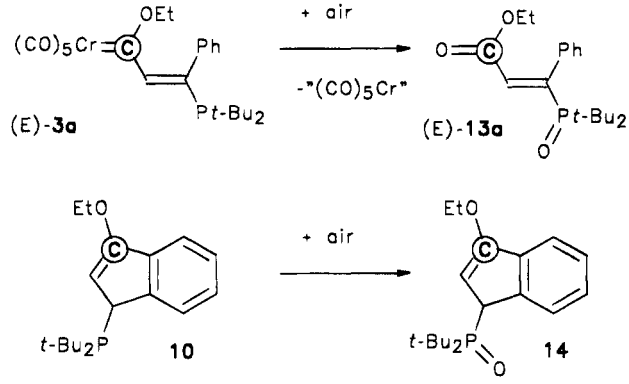
(10) More commonly, indene formation is viewed as occurring *via* a dissociation of carbon monoxide, a subsequent electrocyclic ring closure to a metallocyclohexadiene intermediate, a reductive elimination, and a metal-mediated hydrogen shift (see ref 2).
(11) Mavel, G. *Annu. Rep. NMR Spectrosc.* **1973**, *5b*, 1–350.

Table 1. Product Ratio of Indenes 9–12 Formed on Thermolysis of 3 under Different Reaction Conditions

				reaction condns		
starting material	M	R	yield[a] (%)	time (h)	temp (°C)	9:9':10:12
3a	Cr	*t*-Bu	>90	3	60	4:1:0:0
3a	Cr	*t*-Bu	>90	3	80	0:0:1:0
3a	Cr	*t*-Bu	>90	3	80 (+C_5H_5N)	0:0:0:1
3b	W	*t*-Bu	>90	35	55	1:0:0:0
3b	W	*t*-Bu	>90	1	80	2:0:1:0
3b	W	*t*-Bu	>90	10	80	0:0:1:0
3b	W	*t*-Bu	>90	8	80 (+C_5H_5N)	0:0:0:1
3c	Cr	*c*-C_6H_{11}	>90	2	80	8:0:1:0
3c	Cr	*c*-C_6H_{11}	>90	2	100	0:0:1:0

[a] Total yield of indenes according to ^{1}H NMR spectra. [b] Product ratio of corresponding indenes.

Scheme 5. Oxidation of Phosphinoindenes and (2-Phosphinoethenyl)carbene Complexes



the dissociation of the P–Cr bond. A rearrangement simply by rotation of the C3–P bond of **9/9'** apparently is strongly hindered by the bulkiness of both the $M(CO)_5$ and the *tert*-butyl groups. The rearrangement of **9/9'** to **10** involves a metal-mediated (supposed intramolecular) 1,3 hydrogen shift and is observed at elevated reaction temperatures only (Table 1). The elimination of a pyridine complex **11** leads concomitantly to the generation of **12**.

Oxidation of Phosphines 3 and 12. It is important to note that compounds **12** are readily oxidized in solution on exposure to air within a few hours to the corresponding phosphine oxide **14** (Scheme 5). (2-Phosphinoethenyl)carbene complexes, e.g., (*E*)-**3a**, are stable in the solid state but decompose in solution under the influence of oxygen by formation of the phosphono acrylate, e.g., (*E*)-**13a**.

Crystal Structure Analysis of Indene 10a. Figure 1 shows the molecular structure and Tables 2 and 3 show the experimental data for the crystal structure of **10a**. The Cr–P distance [2.525(2) Å] is significantly longer than it is in compounds of type (*E*)-**7** (Scheme 3) [M = Cr, R = Ph, Cr–P 2.409(8)].[1,12] The coordination geometry at the phosphorus atom corresponds to a slightly distorted tetrahedral structure, with angles ranging from 105.7(2) to 116.7(2) Å. The $Cr(CO)_5$ moiety and the hydrogen atom 3-H are arranged *syn* to each other, in line with expectations, if **10** were generated from **9** by an *intra*molecular metal-induced 1,3 hydrogen shift (see above).

(12) For a compilation of more data, see: Jelinek-Fink, H.; Duessler, E. N.; Paine, R. T. *Acta Crystallogr.* **1987**, *C43*, 635–636.

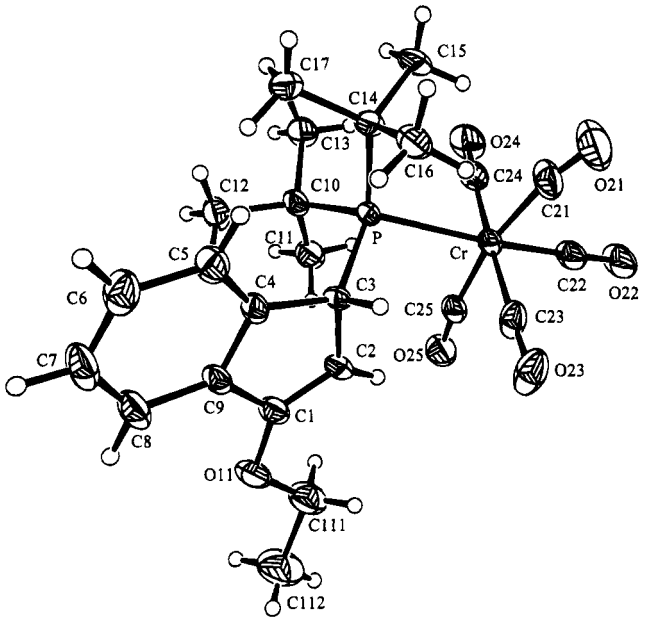


Figure 1. View of the molecular structure of **10a** with selected bond distances (Å) and angles (deg): Cr–P 2.525(2), P–C3 1.893(5), P–C10 1.906(5), P–C14 1.903(6), Cr–P–C3 107.1(2), C10–P–C14 108.9, C3-C2 1.508(7), C3–C4 1.523(7), C2–C1 1.345(7), C4–C9 1.404(7), C1–C9 1.430(8), C1–O11 1.359(6), C10–P–C14 108.9(3), C3–P–Cr 107.1(2), C3–P–C10 106.3(2), C3–P–C14 105.7(2), C14–P–Cr 111.6(2), C10–P–Cr 116.7(2).

Table 2. Crystal Data and Structure Refinement for 10a

identification code	AUM_151
empirical formula	$C_{24}H_{29}CrO_6P$
fw	496.44
temp (K)	223(2) K
wavelength (Å)	0.71073 Å
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell dimens	
a (Å)	9.412(1)
b (Å)	11.455(2)
c(Å)	11.962(2)
α (deg)	89.10(1)
β (deg)	79.09(1)
γ (deg)	88.60(1)
vol (Å^3)	1265.9(3)
Z	2
density (calcd) (mg/m^3)	1.302
abs coeff (mm^{-1})	0.550
F(000)	520
cryst size (mm)	0.2 × 0.2 × 0.15
Θ range for data collection	2.53–26.31°
index ranges	0 ≤ h ≤ 11, −14 ≤ k ≤ 14, −14 ≤ l ≤ 14
no. of reflns collcd	5469
no. of ind reflns	5141 [*R*(int) = 0.058]
refinement method	full-matrix least squares on F^2
data/restraints/params	5137/0/296
goodness of fit on F^2	1.001
final *R* indices [I > 2σ(I)]	$R_1 = 0.063$, $wR^2 = 0.117$
R indices (all data)	$R_1 = 0.231$, $wR^2 = 0.171$
largest diff peak and hole (eÅ^{-3})	
diffractometer	Enraf-Nonius CAD4
programs used	SHELX-86, SHELX-93, ORTEX

Experimental Section

All operations were performed under argon. Solvents were dried by distillation from sodium/benzophenone. ^{1}H NMR and ^{13}C NMR spectra were obtained with Bruker WM 300 spectrometer. Multiplicities were determined by DEPT. Chemical shifts refer to $\delta_{TMS} = 0.00$ ppm. Other analyses: IR Digilab FTS 45; MS, Finnigan MAT 312; elemental analysis, Perkin-Elmer 240 elemental analyser; melting points uncorrected; column chromatography, Merck Kieselgel 100. TLC, Merck DC-Alufolien Kieselgel 60 F 254. R_f values refer to TLC tests.

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

	x	*y*	*z*	*U*(eq)
Cr	1310(1)	2466(1)	8972(1)	50(1)
C(21)	1775(7)	3550(7)	10006(6)	76(2)
O(21)	1889(6)	4237(6)	10669(5)	120(2)
C(22)	−469(8)	2532(6)	9912(5)	64(2)
O(22)	−1576(5)	2571(5)	10529(4)	94(2)
C(23)	797(7)	3782(6)	8126(6)	58(2)
O(23)	397(6)	4540(5)	7651(5)	90(2)
C(24)	1713(7)	1145(7)	9839(6)	62(2)
O(24)	1854(6)	339(5)	10386(4)	91(2)
C(25)	461(7)	1532(6)	8007(5)	51(2)
O(25)	−197(5)	1044(4)	7450(4)	69(1)
P	3818(2)	2299(1)	7771(1)	36(1)
C(10)	4485(6)	773(5)	7282(4)	42(2)
C(11)	3236(7)	102(5)	6989(5)	55(2)
C(12)	5716(7)	773(5)	6238(5)	54(2)
C(13)	5000(7)	92(5)	8248(5)	60(2)
C(14)	5221(6)	2985(5)	8497(4)	41(1)
C(15)	5035(7)	2575(6)	9734(5)	56(2)
C(16)	4958(6)	4311(5)	8470(5)	53(2)
C(17)	6805(6)	2722(5)	7939(5)	56(2)
C(1)	3251(7)	2677(5)	4683(5)	47(2)
O(11)	2611(5)	2328(4)	3820(3)	61(1)
C(111)	1107(9)	2056(7)	4120(6)	79(2)
C(112)	564(10)	1823(8)	3052(7)	126(4)
C(2)	2683(6)	2762(4)	5799(5)	41(1)
C(3)	3803(6)	3198(4)	6431(4)	37(1)
C(4)	5085(6)	3381(5)	5462(5)	39(1)
C(5)	6394(7)	3919(5)	5414(5)	50(2)
c(6)	7364(7)	3995(5)	4378(6)	59(2)
C(7)	6990(8)	3586(6)	3396(6)	62(2)
C(8)	5675(8)	3129(5)	3416(5)	54(2)
C(9)	4722(7)	3036(5)	4432(5)	42(1)

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

1-(*tert*-Butylamino)-4-(di-*tert*-butylphosphino)-2-ethoxynaphthalene (6a) and [(*E*)-*N*-(*tert*-Butyl)-4-(di-*tert*-butylphosphino)-2-ethoxy-4-phenyl-1,3-butadien-1-imine, P–Cr]pentacarbonylchromium [(*E*)-8a] from Chromium Complex (*E*)-3a. (a) NMR experiment. To 50 mg (0.10 mmol) of (3-di-*tert*-butylphosphino-1-ethoxy-3-phenyl-propenylidene)pentacarbonylchromium [(*E*)-**3a**][1] in 1 mL of C_6D_6 and hexamethylbenzene as an internal standard is added 16 mg (0.20 mmol) of *tert*-butyl isocyanide (**4a**) at 20 °C. The initially red solution turns yellow within 1 min. NMR measurements (360 MHz) indicate the presence of a 2:1:2:1 mixture of **6a**, (*E*)-**8a**, $(CO)_5Cr(t\text{-BuNC})$ (**5a**), and unreacted **4a**. After 1 h at 60 °C, the signals of (*E*)-**8a** have disappeared, and signals expected for a 3:3 mixture of **6a** and **5a** are observed. (*E*)-**8a** is hydrolyzed on silica gel and therefore cannot be isolated by chromatography.

(b) Preparation of 6a. To 248 mg (0.50 mmol) of (*E*)-**3a** in 3 mL of cyclohexane is added 83 mg (1.00 mmol) of *tert*-butyl isocyanide (**4a**) with vigorous stirring at 20 °C. The mixture is heated to 60 °C for 1 h to complete the conversion of (*E*)-**8a** into **6a**. Chromatography on silica gel with pentane/dichloromethane (4:1) yields colorless **5a** (125 mg, identified by IR and by comparison of the TLC with authentic material); elution with dichloromethane/pentane (1:1) affords pale yellow **6a** [$R_f = 0.4$ in dichloromethane/pentane (1:1), 185 mg, 96%, colorless crystals from pentane, mp 104 °C].

6a: ^{1}H NMR (C_6D_6): δ 9.35 [1H, dd, ^3J = 7 Hz, ^3J(P,H) = 7, 5-H], 8.62 (1H, d, ^3J = 7 Hz, 8-H), 7.76 [1H, d, ^3J(P,H) = 2 Hz, 3-H], 7.29 and 7.05 (1H each, dd, ^3J = 7 and 7 Hz each, 6-H and 7-H), 3.92 (2H, q, OCH_2), 3.59 (1H, s broad, NH), 1.27 (9H, N*t*-Bu), 1.20 (18H, P*t*-Bu_2), 1.23 (3H, t, CH_3, Et). ^{13}C NMR (C_6D_6): δ 149.8 (Cq, C2), 137.0 [Cq, ^2J(P,C) = 26 Hz, C4], 134.8 [Cq, ^3J(C,P) = 7 Hz, C1], 132.4 (Cq, C9), 130.8 [Cq,

^1J(C,P) = 24 Hz, C10], 127.9 [CH, ^2J(C,P) = 37 Hz, C3]; 126.6, 125.2, 124.1 (CH each, C6–C8), 121.5 [CH, ^3J(C,P) = 4 Hz, C5], 64.8 (OCH_2), 56.0 ($NCMe_3$), 33.4 [Cq, ^1J(P,C) = 22 Hz, $PCMe_3$], 31.8 (CH_3, N*t*-Bu), 30.0 [CH_3, ^2J(C,P) = 15 Hz, P*t*-Bu], 15.6 (CH_3, Et). IR (diffuse reflection): 3330 cm^{-1} [ν(N–H)]. MS (70 eV), *m/e* (%): 388 (40) [M^+ + 1], 387 (50) [M^+], 330 (50), 274 (100) [M^+ – *tert*-Bu – $Me_2C{=}CH_2$], 218 (40), 190 (10). Anal. Calcd for $C_{24}H_{38}NOP$ (387.6): C, 74.38; H, 9.88; N, 3.61. Found: C, 74.43; H, 9.75; N, 3.52.

(*E*)-**8a**: ^{1}H NMR (C_6D_6): δ 7.30 and 7.08 (2:3H, m each, 4-Ph), 7.10 [1H, d, ^3J(P,H) = 8 Hz, 3-H], 3.18 (2H, q, 2-OCH_2), 1.18 [18H, ^3J(C,P) = 12 Hz, P*t*-Bu_2], 1.05 (9H, N*t*-Bu), 0.71 (3H, t, CH_3, Et). ^{13}C NMR (C_6D_6): δ 222.6 [Cq, 1C, ^2J(P,C) = 4 Hz, *trans*-CO, $(CO)_5Cr$], 219.1 [Cq, 4C, ^2J(P,C) = 11 Hz, *cis*-CO, $(CO)_5Cr$], 191.8 (Cq, C1), 155.8 [Cq, ^1J(P,C) = 86 Hz, C4], 141.0 [CH, ^2J(P,C) = 26 Hz, C3], 137.1 [Cq, ^2J(P,C) = 32 Hz, *i*C, 4-Ph]; 128.8, 127.7, 125.3 (2:1:2, CH each, 4-Ph); 113.1 [Cq, ^3J(P,C) = 18 Hz, C2], 67.5 (OCH_2), 61.4 (Cq, $NCMe_3$), 33.0 [Cq, ^1J(P,C) = 22 Hz, $PCMe_3$], 31.3 (CH_3, N*t*-Bu), 31.0 (CH_3, P*t*-Bu_2), 14.8 (CH_3, Et).

1-(*tert*-Butylamino)-4-(di-*tert*-butylphosphino)-2-ethoxynaphthalene (6a) from Tungsten Complex (*E*)-3b. To 63 mg (0.10 mmol) of (3-di-*tert*-butylphosphino-1-ethoxy-3-phenylpropenylidene)pentacarbonyltungsten [(*E*)-**3b**][1] in 1 mL of C_6D_6 is added 16 mg (0.10 mmol) of *tert*-butyl isocyanide (**4a**) at 20 °C. The initially red solution turns yellow within 1 min. ^{1}H NMR measurements (360 MHz) indicate that a clean conversion into a 1:1 mixture of **6a** and $(CO)_5W$(*t*-BuNC) (**5b**) has occurred.

[(*E*)-*N*-(*tert*-Butyl)-4-(di-*tert*-butylphosphino)-2-ethoxy-4-phenyl-1,3-butadien-1-imine, P–Cr]pentacarbonylchromium [(*E*)-8a] from (*E*)-7a and Its Conversion to 6a. To 34 mg (0.05 mmol) of (*E*)-**7a**[1] in 1 mL of C_6D_6 is added 8 mg (0.10 mmol) of **4a**. The initially red solution turns yellow immediately and shows ^{1}H and ^{13}C NMR spectra that are identical with those of (*E*)-**8a** and **5a**. After 1 h at 60 °C, a complete conversion of (*E*)-**8a** into **6a** is indicated by the ^{1}H NMR spectrum.

[(*E*)-*N*-(*tert*-Butyl)-4-(di-*tert*-butylphosphino)-2-ethoxy-4-phenyl-1,3-butadien-1-imine, P–Cr]pentacarbonyltungsten [(*E*)-8b] from (*E*)-7b and Its Conversion to 6a. To 48 mg (0.05 mmol) of (*E*)-**7b**[1] in 1 mL of C_6D_6 is added 8 mg (0.10 mmol) of **4a**. The initially red solution turns yellow immediately and shows ^{1}H NMR signals of (*E*)-**8b** and **5b**. Compound (*E*)-**8b** is stable at 60 °C for at least 1 h according to ^{1}H NMR spectra. After 1 h at 100 °C, a partial conversion (10–20%) of (*E*)-**8b** into **6a** is observed.

(*E*)-**8b**: ^{1}H NMR (C_6D_6): δ 7.35, and 7.03 (2:3H, m each, 4-Ph), 7.22 [1H, d, ^3J(P,H) = 8 Hz, 3-H), 3.28 (2H, q, 2-OCH_2), 1.18 [18H, ^4J(C,P) = 12 Hz, P*t*-Bu_2], 1.07 (9H, N*t*-Bu), 0.65 (3H, t, CH_3, Et).

4-(Di-*tert*-butylphosphino)-1-(cyclohexylamino)-2-ethoxynaphthalene (6b). To 248 mg (0.50 mmol) of (3-di-*tert*-butylphosphino-1-ethoxy-3-phenylpropenylidene)pentacarbonylchromium [(*E*)-**3a**] in 3 mL of cyclohexane is added 109 mg (1.00 mmol) of cyclohexyl isocyanide (**4b**) with vigorous stirring at 20 °C. The mixture is heated to 60 °C for 1 h in order to guarantee a complete conversion of the ketene imine complex of type (*E*)-**8** into **6b**. Chromatography on silica gel with pentane/dichloromethane (4:1) yields colorless **5c** (140 mg, identified by IR and by comparison on TLC with authentic material) and with dichloromethane/pentane (1:1) pale yellow **6b** [R_f = 0.4 in dichloromethane/pentane (1:1), 210 mg, 96%, colorless crystals from pentane, mp 104 °C). Alternatively, **6b** is obtained by the addition of 109 mg (1.00 mmol) of **4b** to 314 mg (0.50 mmol) of (3-di-*tert*-butylphosphino-1-ethoxy-3-phenylpropenylidene)pentacarbonyltungsten [(*E*)-**3b**] at 20 °C in a smooth reaction, as is indicated by the ^{1}H NMR spectrum.

6b: ^{1}H NMR (C_6D_6): δ 9.43 [1H, dd, ^3J = 7 Hz, ^3J(P,H) = 7, 5-H], 8.35 (1H, d, ^3J = 7 Hz, 8-H), 7.82 [1H, d, ^3J(P,H) = 2 Hz, 3-H], 7.38 (2H, m, 6-H and 7-H), 3.95 (2H, q, OCH_2), 3.45 (1H, s broad, NH), 3.25 (1H, m, NCH); 2.00, 1.55, 1.30–0.80 (11H, m, 5 CH_2, C_6H_{11}), 1.28 [18H, d, ^3J(P,H) = 14 Hz, averaged signals of P*t*-Bu_2], 1.23 (3H, t, CH_3, Et). ^{13}C NMR ($CDCl_3$): δ 145.4 (Cq, C2), 136.0 [Cq, ^2J(P,C) = 26 Hz, C4], 133.3 (Cq, C1), 128.5 [CH, ^2J(C,P) = 37 Hz, C3], 128.6 [Cq, ^3J(P,C) = 7 Hz, C9], 126.9 [Cq, ^1J(C,P) = 24 Hz, C10]; 124.5, 123.1, 123.0, 122.9 (CH each, C6 to C8), 121.5 [CH, ^3J(C,P) = 4 Hz, C5], 66.8 (OCH_2), 57.0 (CH N); 34.6, 26.0, and 25.2 (2:2:1, CH_2 each, Cy); 32.7 [Cq, ^1J(P,C) = 22 Hz, $PCMe_3$], 29.7 [6 CH_3, d, dynamically broadened, ^2J(C,P) = 15 Hz, P*t*-Bu_2], 15.2 (CH_3, Et). IR (diffuse reflection): 3344 cm^{-1} [ν(N–H)]. MS (70 eV), *m/e* (%): 413 (40) [M^+], 356 (30), 300 (100) [M – 2 *t*-Bu]. Anal. Calcd for $C_{26}H_{40}NOP$ (413.6): C, 75.51; H, 9.75; N, 3.39. Found: C, 75.55; H, 9.70; N, 3.34.

[1-(Di-*tert*-butylphosphino)-3-ethoxyindene, P–Cr]-pentacarbonylchromium (10a) and [3-(Di-*tert*-butylphosphino)-1-ethoxyindene, P–Cr]pentacarbonylchromium (9a and 9a'). A 248 mg (0.50 mmol) sample of (3-(di-*tert*-butylphosphino)-1-ethoxy-3-phenylpropenylidene)pentacarbonylchromium [(*E*)-**3a**] in 2.5 mL of dry benzene is heated to 60 °C for 3 h. According to ^{1}H NMR spectra, (*E*)-**3a** is consumed completely and a 4:1 mixture of **9a** and **9'a** is formed. **9a** was isolated by crystallization from pentane at –15 °C [R_f = 0.4 in dichloromethane/pentane (1:3), 150 mg, 60%], while **9a'** is accumulated in the mother liquor. Heating of a benzene solution of (*E*)-**3a** (or of **9a** and **9'a**) for 3 h to 80 °C yields mainly **10a** [R_f = 0.4 in dichloromethane/pentane (1:10), yellow crystals from pentane at –45 °C, mp 102 °C, dec].

10a: ^{1}H NMR (C_6D_6): δ 7.81, 7.56, 7.12, 7.04 (1H each; d, d, dd, dd; ^3J = 8 Hz each, 4-H–7-H); 5.81 [1H, dd, ^3J(P,H) = 3 Hz, ^3J = 2 Hz, 2-H], 4.35 [1H, dd, ^2J(P,H) = 8 Hz, ^3J = 2 Hz, 1-H], 3.95, and 3.80 (1H each, m each, diastereotopic OCH_2), 1.23, 1.05 [9H each, d each, ^3J(P,H) = 12 Hz each, diastereotopic *t*-Bu], 1.15 (3H, t, CH_3, Et). ^{13}C NMR (C_6D_6): δ 221.8 [Cq, 1C, ^2J(P,C) = 6 Hz, *trans*-CO, $(CO)_5Cr$], 219.1 [Cq, 4C, ^2J(P,C) = 11 Hz, *cis*-CO, $(CO)_5Cr$], 157.5 [Cq, d, ^3J(P,C) = 8 Hz, C3], 143.8 [Cq, d, ^2J(P,C) = 8 Hz, C8], 142.6 (Cq, C9); 127.7, 126.6, 126.5, and 120.6 (CH each, C4–C7); 103.8 [CH, d, ^2J(P,C) = 4 Hz, C2], 66.4 (OCH_2), 51.2 (CH, C1), 40.0, and 38.9 (Cq each, diastereotopic $PCMe_3$), 31.5, and 30.8 (CH_3 each, diastereotopic P*t*-Bu_2), 15.8 (CH_3, Et). IR (hexane), cm^{-1} (%): 2056.2 (30), 1982.6 (5), 1928.0 (100) [ν(C≡O)]. MS (70 eV), *m/e* (%): 496 (20) [M^+], 468 (10), 440 (5), 412 (30), 384 (25), 356 (60) [M^+ – 5CO], 314 (50), 304 (50) [356 – Cr], 272 (50), 248 (50), 247 (50), 159 (90), 131 (100) [indenone]. Anal. Calcd for $C_{24}H_{29}CrO_6P$ (496.5): C, 58.06; H, 5.89. Found: C, 58.23; H, 5.97.

9a: ^{1}H NMR (C_6D_6): δ 8.18, 7.40, 7.21, 7.03 (1H each; d, d, dd, dd; ^3J = 8 Hz each, 4-H–7-H); 6.87 [1H, dd, ^3J(P,H) = 5.5 Hz, ^3J = 2 Hz, 2-H], 5.03 (1H, d, ^3J = 2 Hz, 1-H), 3.28, and 3.15 (1H each, m each, diastereotopic OCH_2), 1.20 (18H, 2 *t*-Bu), 1.15 (3H, t, CH_3, Et). ^{13}C NMR (C_6D_6): δ 222.6 [Cq, 1C, ^2J(P,C) = 6 Hz, *trans*-CO, $(CO)_5Cr$], 219.1 [Cq, 4C, ^2J(P,C) = 11 Hz, *cis*-CO, $(CO)_5Cr$], 147.3 (CH, C2), 143.8 [Cq, ^1J(P,C) = 20 Hz, C3], 143.6 (Cq, C8), 139.1 [Cq, ^1J(P,C) = 9 Hz, C9]; 128.4, 126.9, 125.4, 124.7 [CH each, C4–C7]; 83.0 [CH, ^3J(P,C) = 4 Hz, C1], 62.0 (OCH_2), 38.8 and 38.6 [Cq each, ^1J(P,C) = 15 Hz each, $PCMe_3$], 31.9 and 31.8 (3 CH_3 each, P*t*-Bu), 16.5 (CH_3, Et). IR (hexane), cm^{-1} (%): 2057.7 (20), 1972.0 (5), 1941.2 (80), 1926.5 (100) [ν(C≡O)]. MS (70 eV), *m/e* (%): 496 (5) [M^+], 412 (5), 384 (5), 356 (30) [M^+ – 5CO], 320 (30) [ligand + O ?], 304 (10) [356 – Cr], 291 (20) [320 – Et], 247 (60) [304 – tBu], 159 (95), 131 (100) [indenone]. Anal. Calcd for $C_{24}H_{29}CrO_6P$ (496.5): C, 58.06; H, 5.89. Found: C, 58.18; H, 5.94.

9'a: ^{1}H NMR (C_6D_6): δ 7.94, 7.48, 7.23, 7.08 (1H each; d, d, dd, dd; ^3J = 8 Hz each, 4-H–7-H); 6.73 [1H, dd, ^3J(P,H) = 2.5 Hz, ^3J = 2 Hz, 2-H], 5.14 (1H, d, ^3J = 2 Hz, 1-H), 3.39 and 3.25 (1H each, m each, diastereotopic OCH_2), 1.25 (18H, 2 *t*-Bu), 1.11 (3H, t, CH_3, Et). ^{13}C NMR (C_6D_6): δ 219.1 and 218.1 [Cq each, d each, ^2J(P,C) = 8.5 Hz each, $(CO)_5Cr$], 143.8 (CH, C2), 143.0 [Cq, ^1J(P,C) = 18 Hz, C3], 142.9 (Cq, C8), 142.0 (Cq, C9) = 9 Hz, C9]; 128.6, 127.8, 126.2, 123.8 [CH each, C4–

C7]; 84.0 [CH, ^3J(P,C) = 8 Hz, C1], 62.2 (OCH_2), 39.4 and 38.6 (Cq each, diastereotopic P*C*Me$_3$), 30.8 and 33.0 (3 CH_3 each, P*t*-Bu), 16.5 (CH_3, Et).

[1-(Di-*tert*-butylphosphino)-3-ethoxyindene, P−W]pentacarbonyltungsten (10b) and [3-(Di-*tert*-butylphosphino)-1-ethoxyindene, P−W]pentacarbonyltungsten (9b) by Thermolysis of (*E*)-3b. Thermolysis of [3-(di-*tert*-butylphosphino)-1-ethoxy-3-phenyl-propenylidene]pentacarbonyltungsten [(*E*)-**3b**] in an inert solvent leads to mixtures of varying composition, depending on the reaction conditions.

(a) NMR Experiments. A ^{1}H NMR spectrum of a solution of 32 mg (0.01 mmol) (*E*)-**3b** in 1 mL of C_6D_6 after 35 h at 55 °C shows signals of **9b** only. For different product composition, see Table 1.

(b) Preparation of 9b. A 314 mg (0.50 mmol) sample of (*E*)-**3b** in 3 mL of heptane is heated for 35 h to 55 °C. Chromatography on silica gel with pentane/dichloromethane (3:1) yields colorless **9b** [R_f = 0.4 in pentane/dichloromethane (3:1), 285 mg, 91%, pale yellow crystals, mp 98 °C].

(c) Preparation of 10b. A 314 mg (0.50 mmol) sample of (*E*)-**3b** in 3 mL of heptane is heated for 10 h to 80 °C. Chromatography on silica gel with pentane/dichloromethane (3:1) yields colorless **10b** [R_f = 0.4 in pentane/dichloromethane (3:1), 270 mg, 86%, pale yellow crystals, mp 140 °C, dec) and yellow **9b.**

10b: ^{1}H NMR (C_6D_6): δ 7.87 (1H, d, ^3J = 7.5 Hz, 8-H), 7.56 (1H, dd, ^3J = 7 Hz, ^4J = 1.5 Hz, 4-H), 7.12 (1H, dd, ^3J = 7.5, 7.5 Hz, 5-H), 7.05 (1H, ddd, ^3J = 7, 7.5 Hz, ^4J = 1.5, 6-H), 5.78 [1H, dd, ^3J(P,H) = 3 Hz, ^3J = 2 Hz, 2-H], 4.40 [1H, dd, ^2J(P,H) = 8 Hz, ^3J = 2 Hz, 1-H], 3.93 and 3.80 (1H each, m each, diastereotopic OCH_2), 1.21 and 1.06 [9H each, d each, ^3J(P,H) = 13 Hz each, diastereotopic P*t*-Bu$_2$], 0.95 (3H, t, CH_3, Et). ^{13}C NMR (C_6D_6): δ 199.8 [4C, d, ^3J(P,C) = 6 Hz, *cis*-CO, $(CO)_5$W], 198.0 [1C, d, ^3J(P,C) = 11 Hz, *trans*-CO, $(CO)_5$W], 157.5 [Cq, d, ^3J(P,C) = 6 Hz, C3], 142.3 [Cq, d, ^2J(P,C) = 7 Hz, C8], 141.4 (Cq, C9); 128.8, 128.6, 127.0, 119.8 (CH each, C4−C7); 103.8 (CH, C2), 65.8 (OCH_2), 51.2 (CH, ^1J(P,C) = 7 Hz, C1), 40.0 and 39.0 [Cq each, ^1J(P,C) = 6 and 7 Hz, diastereotopic P*C*Me$_3$], 31.6 and 31.4 (CH_3 each, diastereotopic P*t*-Bu$_2$), 15.0 (CH_3, Et). MS (70 eV, ^{184}W, *m/e* (%): 628 (20) [M$^+$], 488 (20) [M$^+$ − 5CO], 304 (30) [488 − W], 247 (30), 191 (30), 159 (80), 131 (100). IR (hexane), cm^{-1} (%): 2067.3 (20), 1936.0 (100) [ν(CO)]. Anal. Calcd for $C_{24}H_{29}O_6PW$ (628.3): C, 45.88; H, 4.65. Found: C, 45.97; H, 4.55.

9b: ^{1}H NMR (C_6D_6): δ 8.17, 7.40, 7.19, 7.01 (1H each; d, d, dd, dd; 4-H−7-H); 6.87 [2-H, dd, ^3J(P,H) = 6 Hz, ^3J = 2 Hz, 2-H], 5.05 (1H, d, ^3J = 2 Hz, 1-H), 3.30 and 3.25 (1H each, m each, diastereotopic OCH_2), 1.25 and 1.20 (9H each, d each, ^3J(P,H) = 14 Hz each, diastereotopic P*t*-Bu$_2$), 1.15 (3H, t, CH_3, Et). ^{13}C NMR (C_6D_6): δ 218.6 [Cq, 4C, ^2J(P,C) = 8 Hz, *cis*-CO, $(CO)_5$W], 198.3 [Cq, 1C, ^2J(P,C) = 21 Hz, *trans*-CO, $(CO)_5$W], 147.5 [CH, ^2J(P,C) = 6 Hz, C2], 143.8 (Cq, C8), 143.6 [Cq, ^1J(P,C) = 17 Hz, C3], 138.5 [Cq, ^2J(P,C) = 15 Hz, C9]; 128.3, 126.9, 126.2, 124.7 [CH each, C4−C7]; 83.0 [CH, ^3J(P,C) = 9 Hz, C1), 62.0 (OCH_2), 38.3 and 38.1 [Cq each, ^1J(P,C) = 14 Hz each, diastereotopic P*C*Me$_3$], 31.3 and 31.1 [CH_3 each, ^2J(P,C) = 14 Hz, diastereotopic C*Me*$_3$], 16.3 (CH_3, Et). IR (hexane), cm^{-1} (%): 2067.7 (20), 1973.2 (5), 1940.2 (90), 1925.7 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m/e* (%): 628 (20) [M$^+$], 572 (5), 516 (20), 488 (20) [M$^+$ − 5CO], 304 (30) [488 − W], 247 (30), 191 (60), 163 (40), 57 (100). Anal. Calcd for $C_{24}H_{29}O_6PW$ (628.3): C, 45.88; H, 4.65. Found: C, 46.12; H, 4.63.

[3-(Dicyclohexylphosphino)-1-ethoxyindene, P−Cr]pentacarbonylchromium (9c) and [1-(Dicyclohexylphosphino)-3-ethoxyindene, P−Cr]pentacarbonylchromium (10c). A 274 mg (0.50 mmol) sample of [3-dicyclohexylphosphino)-1-ethoxy-3-phenylpropenylidene]pentacarbonylchromium [(*E*)-**3c**] in 4 mL of heptane is heated for 2 h to 80 °C. The ^{1}H NMR spectra indicate a clean conversion of (*E*)-**3c** into a 8:1 mixture of **9c** and **10c**. After 2 h at 100 °C, compound **10c** is observed as the only product.

10c: ^{1}H NMR (C_6D_6): δ 7.61, 7.21, 7.12, 7.02 (1H each; d, d, dd, dd; ^3J = 8 Hz each, 4-H−7-H); 5.50 [1H, dd, ^3J(P,H) = 3 Hz, ^3J = 2 Hz, 2-H], 4.15 [1H, dd, ^2J(P,H) = 8 Hz, ^3J = 2 Hz, 1-H], 3.80 and 3.65 (1H each, m each, diastereotopic OCH_2), 2.30 and 2.25 [1H each, d each, ^3J(P,H) = 12 Hz each, diastereotopic CHP, Cy]; 1.85, 1.66, 1.52, 1.20 (2:8:8:2, m each, CH_2, Cy), 1.05 (3H, t, CH_3, Et). ^{13}C NMR (C_6D_6): δ 222.8 [Cq, 1C, ^2J(P,C) = 6 Hz, *trans*-CO, $(CO)_5$Cr], 219.0 [Cq, 4C, ^2J(P,C) = 13 Hz, *cis*-CO, $(CO)_5$Cr], 158.6 [Cq, C3], 142.5 [Cq, d, ^2J(P,C) = 8 Hz, C8], 141.1 (Cq, C9); 127.6, 126.4, 125.0, and 120.2 (CH each, C4−C7); 100.0 [CH, d, ^2J(P,C) = 4 Hz, C2], 65.6 (OCH_2), 45.7 (CH, C1), 39.3 and 39.1 (CH each, diastereotopic CHP); 38.5, 36.6, 36.4, 35.3, 35.2 (CH_2 each, 2 Cy); 14.9 (CH_3, Et). IR (hexane), cm^{-1} (%): 2056.0 (30), 1982.6 (5), 1928.0 (100) [ν(C≡O)]. MS (70 eV), *m/e* (%): 548 (20) [M$^+$], 520 (10), 464 (40), 436 (30), 409 (50), 408 (60) [M$^+$ − 5CO], 356 (30) [408 − Cr], 327 (50) [356 − Et], 245 (30) [327 − C_6H_{10}], 131 (100). Anal. Calcd for $C_{28}H_{33}CrO_6P$ (548.5): C, 61.31; H, 6.06. Found: C, 61.44; H, 6.28.

9c: ^{1}H NMR (C_6D_6): δ 7.72, 7.30, 7.21, 7.13 (1H each; d, d, dd, dd; ^3J = 8 Hz each, 4-H−7-H); 7.02 [1H, dd, ^3J(P,H) = 5.5 Hz, ^3J = 2 Hz, 2-H], 5.00 (1H, d, ^3J = 2 Hz Hz, 1-H), 3.26 and 3.16 (1H each, m each, diastereotopic OCH_2), 2.60 (2H, m, diastereotopic CHP); 2.10, 1.80, 1.60, 1.20 (4:6:6:4, CH_2 of Cy); 1.05 (3H, t, Et). IR (hexane), cm^{-1} (%): 2056.7 (20), 1974.3 (5), 1925.2 (100) [ν(C≡O)].

1-(Di-*tert*-butylphosphino)-3-ethoxyindene (12) from (*E*)-3a or (*E*)-3b. (a) NMR experiment. A 25 mg (0.05 mmol) sample of [3-(di-*tert*-butylphosphino)-1-ethoxy-3-phenylpropenylidene)pentacarbonylchromium [(*E*)-**3a**] in 1 mL of C_6D_6, 5 mg (0.05 mmol) of pyridine, and hexamethylbenzene as an internal standard is heated to 80 °C for 2 h. The ^{1}H NMR spectrum indicates a clean conversion of (*E*)-**3a** into **12** (>90%) and $(CO)_5Cr(C_5H_5N)$ **11a** [δ = 7.91, 6.55, and 6.02, 2:1:2H, m each]. A 32 mg (0.05 mmol) sample of [3-(di-*tert*-butylphosphino)-1-ethoxy-3-phenylpropenylidene]pentacarbonyltungsten [(*E*)-**3b**] and 5 mg of pyridine at 80 °C for 8 h give **12** (>90%) and $(CO)_5W(C_5H_5N)$ **11b** [δ = 8.05, 6.95 and 6.04, 2:1:2H, m each].

(b) Preparation of 12. A 248 mg (0.50 mmol) sample (*E*)-**3a** in 4 mL of heptane and 45 mg (0.50 mmol) of pyridine is heated for 1.5 h to 80 °C. **11a** forms yellow crystals at −15 °C, which are removed by centrifugation after 12 h. **12** separates from pentane at −45 ° C in yellowish crystals, mp 88 °C. Solutions of **12** are sensitive to oxidation by air.

12: ^{1}H NMR (C_6D_6): δ 7.92, 7.68, 7.20 (1:1:2H, m each, 4-H−7-H); 5.56 (1H, d, ^3J = 2 Hz, 2-H], 3.84 (2H, m, diastereotopic OCH_2), 3.70 [1H, dd, ^2J(P,H) = 2 Hz, ^3J = 2 Hz, 1-H], 1.29 and 0.93 [9H each, d each, ^3J(P,H) = 11 Hz each, diastereotopic *t*-Bu], 1.21 (3H, t, CH_3, Et). ^{13}C NMR (C_6D_6): δ 157.8 (Cq, C3), 148.1 [Cq, d, ^2J(P,C) = 16 Hz, C8], 138.9 [Cq, d, ^3J(P,C) = 4 Hz, C9]; 126.6, 126.1, 125.2, 119.1 (CH each, C4−C7); 103.5 [CH, d, ^2J(P,C) = 4 Hz, C2], 65.3 (OCH_2), 43.0 [CH, d, ^1J(P,C) = 43 Hz, C1], 34.1 and 32.3 [Cq each, d each, ^1J(P,C) = 32 and 26 Hz, diastereotopic P*C*Me$_3$], 30.8 and 30.2 [CH_3 each, d each, ^2J(P,C) = 14 and 13 Hz, diastereotopic P(C*Me*$_3$)], 14.9 (CH_3, Et). MS (70 eV), *m/e* (%): 304 (10) [M$^+$], 247 (80) [M − *t*-Bu], 191 (50), 159 (100) [M − *t*-Bu$_2$P], 131 (100). Anal. Calcd for $C_{19}H_{29}OP$ (304.4): C, 74.97; H, 9.60. Found: C, 74.75; H, 9.36.

1-(Di-*tert*-butylphosphono)-3-ethoxyindene (14) by Oxidation of 12 on Air. A 30 mg (0.10 mmol) sample of *1*-di-*tert*-butylphosphino-3-ethoxyindene (**12**) in 1 mL of C_6D_6 and hexamethylbenzene as an internal standard is exposed to air for 30 h at 20 °C. The ^{1}H NMR spectrum indicates that a clean conversion into **14** (>90%) has occurred. **14** separates from pentane at −45 ° C in yellowish crystals. ^{1}H NMR (C_6D_6): δ 8.63, 7.71, 7.20 (1:1:2H, m each, 4-H−7-H); 5.16 [1H, dd, ^3J = 2 Hz, ^3J(P,H) = 2 Hz, 2-H], 4.06 [1H, dd, ^2J(P,H) = 22 Hz, ^3J = 2 Hz, 1-H], 3.85 (2H, m, diastereotopic OCH_2), 1.55 and 1.10 [9H each, d each, ^3J(P,H) = 25 Hz each, diastereotopic *t*-Bu], 1.21 (3H, t, CH_3, Et). ^{13}C NMR (C_6D_6): δ 154.3 (Cq, C3), 143.2

[Cq, d, ^2J(P,C) = 4 Hz, C8], 136.0 (Cq, C9); 127.4, 126.8, 124.8, 118.4 (CH each, C4–C7); 97.4 (CH, C2), 64.9 (OCH_2), 45.5 [CH, d, ^1J(P,C) = 33 Hz, C1], 38.1 and 37.0 [Cq each, d each, ^1J(P,C) = 37, 33 Hz, diastereotopic P*C*Me$_3$], 30.6 and 27.2 [CH_3 each, d each, ^2J(P,C) = 11 Hz, diastereotopic P(C*Me*$_3$)], 14.6 (CH_3, Et). IR (diffuse reflection), cm^{-1} (%): = 1176 (100) [(C—O) and/or (P=O)]. MS (70 eV), *m/e* (%): 320 (10) [M^+], 291 (10) [M − Et], 159 (100) [M − *t*-Bu_2PO], 131 (50) [150 − CO]. Anal. Calcd for $C_{19}H_{29}O_2P$ (320.4): C, 74.97; H, 9.60. Found: C, 75.00; H, 9.75.

(*E*)-Ethyl 3-(di-*tert*-butylphosphono)propenoate [(*E*)-13] by Oxidation of (*E*)-3a on Air. A 25 mg (0.05 mmol) sample of [3-(di-*tert*-butylphosphino)-1-ethoxy-3-phenylpropenylidene]pentacarbonylchromium [(*E*)-**3a**] in 1 mL of C_6D_6 and hexamethylbenzene as an internal standard is exposed to air for 30 h at 20 °C. The mixture is centrifuged, and a ^1H NMR spectrum is taken from the supernatant solution, which indicates a clean conversion of (*E*)-**3a** into (*E*)-**13** (>90%). Compound (*E*)-**13** separates from pentane at −45 ° C in yellowish crystals, mp 87 °C. ^1H NMR (C_6D_6): δ 7.20, 7.05, and 7.00 (2:1:2H, m each, Ph); 7.20 [1H, d, ^3J(P,H) = 15 Hz, 2-H], 3.96 (2H, q, OCH_2), 1.17 [18H, d, ^2J(P,H) = 13 Hz, P*t*-Bu_2], 0.68 (3H, t, CH_3, Et). MS (70 eV), *m/e* (%): 337 (10) [M^+ + 1], 279 (5) [M − *t*-Bu], 263 (5), 251 (70) [279 − $H_2C{=}CH_2$], 195 (100) [251 - − C_4H_8], 57 (40), 41 (50). IR (diffuse reflection), cm^{-1} (%): = 1728 (100) [(C=O)], 1165 (100) [(C—O) and/or (P=O)]. Anal. Calcd for $C_{19}H_{29}O_3P$ (336.4): C, 67.84; H, 8.69. Found: C, 67.93; H, 8.80.

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Supplementary Material Available: For **10a**, tables of crystal data and details of data collection, interatomic distances and angles, final thermal parameters, and hydrogen positional parameters (8 pages). Ordering information is given on any current masthead page.

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