°C dec; ^{1}H NMR δ 7.81–7.65 (m, 7 H), 7.48–7.42 (m, 5 H), 7.33–7.16 (m, 19 H), 7.05 (d, 2 H, J = 8.3 Hz), 5.68 (s, 1 H); ^{13}C NMR 146.5 (quaternary), 144.6 (quaternary), 144.4 (quaternary), 143.7 (quaternary), 141.5 (quaternary), 141.2 (quaternary), 133.3 (quaternary), 132.9 (quaternary), 132.1 (quaternary), 131.7 (quaternary), 131.2, 130.9, 129.5, 128.6, 128.33, 128.29, 128.0, 127.9, 127.8, 127.5, 127.2, 16.5, 126.4, 126.0, 125.97, 125.8, 125.6, 64.7 (quaternary), 56.5 ppm; MS(CI) *m/e* 604 (M + NH_4^+). Anal. Calcd for $C_{46}H_{34}$: C, 94.16; H, 5.84. Found: C, 94.10; H, 5.85.

Reaction of 7a (Ar = 4-*tert*-Butylphenyl) with DABCO and Hg. A solution of the propyne **7a** (56 mg, 0.115 mmol) in 10 mL of dry, degassed THF was treated with Hg metal (106 mg, 0.53 mmol) and DABCO (86 mg, 0.767 mmol). The mixture was heated in a sealed tube at 70 °C for 22 h. The tube was then opened and the mixture was filtered. By ^{1}H NMR, the crude reaction showed no methine proton characteristic of rearranged dimer. Concentration in vacuo and column chromatography of the residue (flash silica gel; gradient, 2.5–50% benzene/hexane) gave 14.7 mg (30%) of bis[β-naphthyl(4-*tert*-butylphenyl)methyl] peroxide: mp 181–183 °C dec; ^{1}H NMR δ 7.74 (d, 1 H, J = 7.5 Hz), 7.60–7.58 (m, 3 H), 7.39 (m, 2 H), 7.27 (dd, J = 8.7, 1.8 Hz), 7.21 (d, 4 H, J = 8.6 Hz), 7.15 (d, 4 H, J = 8.6 Hz), 1.30 (s, 18 H).

Isomerization of Alkyne 7 to Propadiene 5 with Alumina. Alkyne **7a** (11 mg, 0.030 mmol) was added as a solid in one portion to 389 mg of basic alumina (Brockman activity I, further activated by heating at 400 °C at 0.05 mmHg for 24 h) suspended in 0.7 mL of dry toluene (or petroleum ether) at −20 °C. The resulting mixture was vigorously stirred at −20 °C for 25 min. By TLC, the alkyne was consumed and a slightly higher R_f UV-active spot was present (10% benzene/hexane). Cold THF (<−20 °C) was then added and the solvent was decanted from the alumina via cannula. The solvent was removed in vacuo to give pure propadiene as a clear oil. Recrystallization from THF/petroleum ether (−80 °C) gave a white solid: ^{1}H NMR ($CDCl_3$, −25 °C) δ 7.45–7.20 (m, 15 H), 6.92 (s, 1 H), 6.67 (d, 1 H, J = 13.7 Hz); ^{13}C NMR ($CDCl_3$, −25 °C), 209.3, 135.7, 135.3, 134.1, 130.9, 128.5, 128.4, 128.0, 127.6, 127.3, 113.0, 108.3, 94.7 ppm.

EPR Spectra of β-Naphthyldiphenylmethyl Radical 6. A. From Allene 7a. To a suspension of activated basic alumina (2.0 g) in 2.5 mL of dry toluene at −20 °C was added **7a** (34 mg, 0.091 mmol) in one portion as a solid. This mixture was vigorously stirred until TLC showed no residual alkyne (10 min). The reaction was diluted with 2.5 mL of cold (−20 °C) toluene. The supernatant liquid was transferred to an appratus consisting of two interconnected Schlenk tubes, one of which was further connected to a vacuum manifold and to an adaptor leading to an EPR cell (Wilmad glass flat cell, WG-812-Q-Suprasil). The bulb containing the allene **5** was isolated from the vacuum manifold, and the second bulb was charged with mercury metal (0.29 g, 1.45 mmol). The mercury metal was added to the toluene solution of **5**, and the yellow mixture was stirred at room temperature for 19.5 h in the dark. The resulting yellow-brown mixture was decanted into the second bulb containing 19 mL of dry, degassed toluene. The solution of **6** was poured into the EPR cell and its EPR spectrum was taken (radical concentration is 5 mM if the dimer of **6** is 100% dissociated). More fine structure was resolved if this solution was diluted 10-fold. The EPR of this 0.5 mM solution is shown in Figure 2.

B. From β-Naphthyldiphenylmethyl Chloride. Via the procedure described for the preparation of **6** from the allene **5**, reaction of β-naphthyldiphenylmethyl chloride (freshly recrystallized from petroleum ether; 33 mg, 0.10 mmol) gave an EPR signal identical with that in Figure 2. The intensity of the spectra obtained from **5** and from the triarylmethyl halide was the same within experimental error (±10%).

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Synthesis, Structure, and Reactivity of (Phosphoranylidenephosphine)pentacarbonyltungsten Complexes. Another Access to the Phosphorus–Carbon Double Bond

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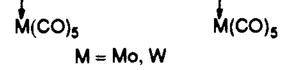
Contribution from the Laboratoire de Chimie du Phosphore et des Métaux de Transition, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France. Received August 4, 1989

Abstract: The reaction of trialkylphosphines with 7-phosphanorbornadiene $PW(CO)_5$ complexes affords the corresponding phosphoranylidenephosphine complexes $R^1_3P{=}P(R){\rightarrow}W(CO)_5$. One such complex (R = CO_2Et, R^1 = Et) has been investigated by X-ray crystal structure analysis. It shows a zwitterionic character with a long P=P bond (2.156 (2) Å). These phosphoranylidenephosphine complexes cleanly react at room temperature with aldehydes to give the corresponding phosphaalkene complexes via a "phospha-Wittig" reaction. These phosphaalkene complexes are either isolated as such or trapped by MeOH, dimethylbutadiene, or benzoic acid.

We have recently developed what we called the "phospha-Wittig" reaction that directly converts a carbonyl compound into a phosphaalkene complex[1-3] (eq 1). In this scheme, the complexing group serves to stabilize both the starting phosphorylphosphine and the final phosphaalkene. Without it, both species are unstable with "ordinary" (i.e., neither bulky nor conjugating) substituents. Stricto sensu, this phospha-Wittig reaction is, in fact, a transposition of the Wittig–Horner synthesis of olefins. It was tempting to generalize this transposition to the genuine Wittig reaction itself. For that purpose, it was necessary to devise a general access to phoshoranylidenephosphines. Indeed, at the beginning of our work, only a few such compounds were known,[4-7] some of which are listed here. Their syntheses obviously depend on either the electron-accepting properties or the steric bulk of



$$R^1R^2CO + (EtO)_2P(O)-\underset{\underset{M(CO)_5}{\downarrow}}{\bar{P}}R \longrightarrow R^1R^2C{=}\underset{\underset{M(CO)_5}{\downarrow}}{P}R + (EtO)_2PO_2^- \quad (1)$$

M = Mo, W

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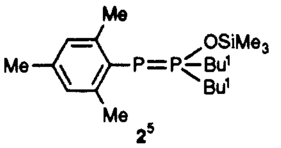
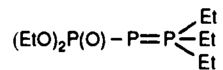
$CF_3P{=}PMe_3$ **1**[4]



2[5]



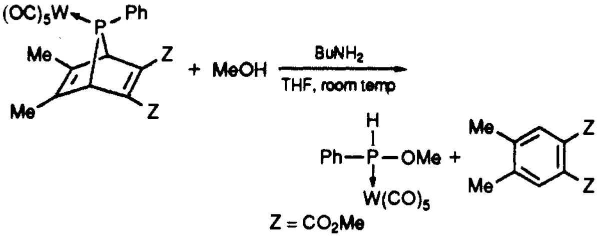
$(EtO)_2P(O)-P{=}PEt_3$

3[6]

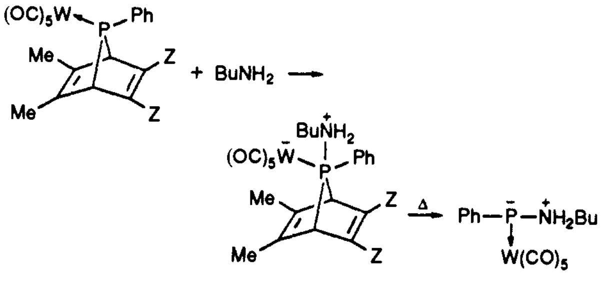
the substituents. Besides, they were never reported to react with carbonyl compounds, probably due to an excessive stabilization. In this work, we describe a method that allows us to build such species in the coordination sphere of tungsten without limitation on the phosphinidene substituent. Due to the use of ordinary substituents, these species are far more reactive than those already mentioned, and they become able to react with carbonyl compounds.

Results and Discussion

At the inception of this work, we remarked that basic amines catalyze the decomposition of 7-phosphanorbornadiene complexes[8] as shown in eq 2. The decomposition of the 7-phosphanorbornadiene complex takes place rapidly at room temperature whereas, without catalyst, such a reaction occurs only above 100 °C.[9] We interpreted this result as implying the transient formation of a Lewis acid-base adduct between the terminal phosphinidene complex and the amine (eq 3). A similar adduct had indeed been characterized by Cowley.[10]

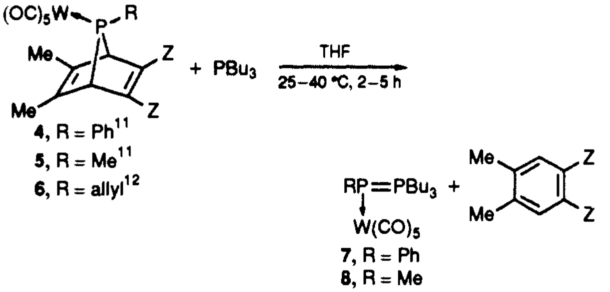


(2)



(3)

As a logical extension of this preliminary finding, we started to investigate the reaction of 7-phosphanorbornadiene complexes with basic trialkylphosphines. ^{31}P NMR spectroscopy allowed us to monitor the rapid and quantitative formation of the expected phosphoranylidenephosphine complexes (eq 4). These species are very reactive, and their purification proved to be difficult. They were mainly characterized by mass and ^{31}P NMR spectroscopy.



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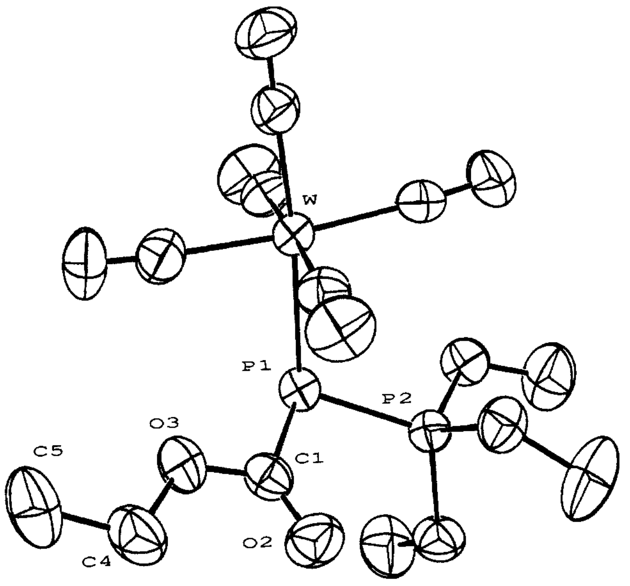
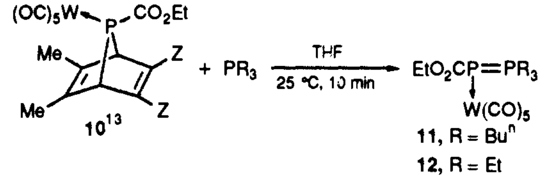


Figure 1. ORTEP drawing of one molecule of **12**. Vibrational ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Principal bond distances (Å): $W-P_1$, 2.603 (1); P_1-P_2, 2.156 (2); P_1-C_1, 1.850 (4); O_2-C_1, 1.201 (5); O_3-C_1, 1.327 (5); O_3-C_4, 1.458 (6); C_4-C_5, 1.490 (9). Selected bond angles (deg): $W-P_1-P_2$, 109.69 (5); $P_2-P_1-C_1$, 95.2 (1); $P_1-C_1-O_2$, 127.5 (4); $P_1-C_1-O_3$, 109.1 (3); $O_2-C_1-O_3$, 123.3 (4); $W-P_1-C_1$, 107.0 (1).

They show huge $^1J(P-P)$ coupling constants ca. 400 Hz in the same range as free phosphoranylidenephosphines.[5,6] The phosphinidene phosphorus appears at high fields (−100 to −145 ppm), although the shifts are far less impressive than in the free species (ca. −200 ppm[5,6]). In order to fully characterize these compounds, we decided to impart some extra stability to the P=P double bond by using an electron-attracting substituent. The ethoxycarbonyl substituent proved to be suitable (eq 5).



(5)

It was possible to purify **11** and **12** by rapid chromatography on silica gel. Compound **12** gave suitable crystals for X-ray analysis. The most significant data are given in the caption of Figure 1. The compound clearly has a zwitterionic character: $[EtO_2C\text{-}P^-\text{-}^+PEt_3]W(CO)_5$. The P_1-P_2 bond (2.156 (2) Å) is closer to a single (ca. 2.24 Å) than to a double bond (ca. 2.03 Å[14]). The $P_2-P_1-C_1-O_2$ unit is planar, suggesting some interaction between O_2 and P_2. Indeed, P_2 is only 0.099 (1) Å outside of the $P_1-C_1-O_2-O_3$ plane. This interaction is probably electrostatic since no conjugation appears between the carbonyl and P_1-P_2 bonds: P_1-C_1 has a normal single-bond length (1.850 (4) Å). Finally, the P_1-W bond appears to be weaker than in classical $R_3P-W(CO)_5$ complexes (2.601 (3) versus ca. 2.50 Å).

Even though compound **12** is not completely representative of the class (for example, the $^1J(P-P)$ coupling constant is lower than usual at 361.3 Hz), we feel that the zwitterionic nature of the phosphorus-phosphorus bond in these phosphoranylidenephosphine complexes is well established. In turn, this polarization of the P=P bond suggests some parallelism between the chemical behaviors of these species and of the so-called phospha-Wittig reagents.[1-3] A rapid investigation of the reactivity of **7–9**, **11**, and **12** toward carbonyl compounds showed that **11** and **12** are un-

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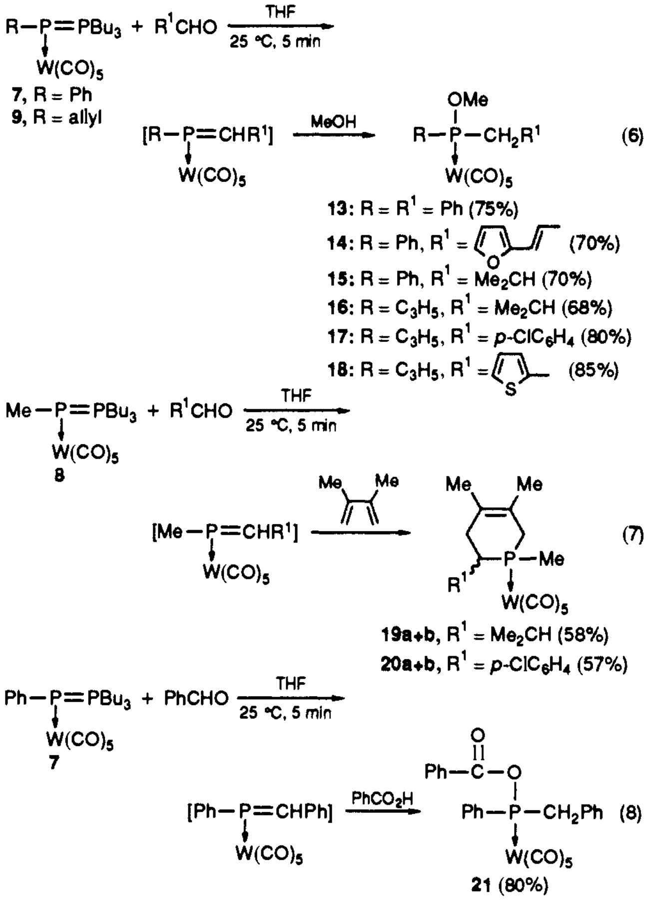
reactive but that **7**–**9** do react. The reactions of **7**–**9** with ketones are sluggish, and the expected phosphaalkenes decompose under the thermal conditions that are needed to promote the conversion. On the contrary, **7**–**9** cleanly react with aldehydes at room temperature. As in our preceding work,[1-3] the very reactive 1,2-disubstituted phosphaalkenes thus produced were trapped in situ by reaction with methanol, 2,3-dimethylbutadiene, or benzoic acid (eqs 6–8). In the synthesis of **15**, the intermediate phosphaalkene is sufficiently stable to be isolated. It has already been described in our preceding work.[2] In the synthesis of **16**, we were able to monitor the formation of the transient phosphaalkene by ^{31}P NMR spectroscopy ($\delta(^{31}P)$ = +195.6, +188.3 ppm).



If we compare the two versions of the phospha-Wittig reaction, it is quite clear that the first one[1-3] that uses the phosphoryl phosphide anions is effective with a wider range of carbonyl compounds due to the relatively high nucleophilicity of the anionic phosphorus. On the other hand, the second one (this work) with the use of the phosphoranylidenephosphines has a broader scope for the substituents at phosphorus. Indeed, very versatile techniques have been devised for introducing a variety of substituents at the bridge phosphorus of 7-phosphanorbornadiene complexes.[13] Thus, these two versions of the phospha-Wittig reaction can be viewed as complementary.

Experimental Section

NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C and on a Bruker WP 80 SY spectrometer operating at 32.44 MHz for ^{31}P. Chemicals shifts are expressed in parts per million downfield from internal TMS (^{1}H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Coupling constants are expressed in hertz. Mass spectra were obtained at 70 eV with a Shimadzu GC-MS QP 1000 instrument by the direct inlet method. Infrared spectra were recorded with a Perkin-Elmer Model 297 spectrometer. Elemental analyses were performed by the Service d'analyse du CNRS, Gif-sur-Yvette, France. Silica gel (70–230 mesh) was used for chromatographic separations. All commercially available reagents were used as received from the suppliers.

Synthesis of (Phosphoranylidenephosphine)pentacarbonyltungsten Complexes (7–9, 11, 12). To a solution of 2.2 mmol phosphanorbornadiene complex (**4**–**7**, **10**) in 10 mL of THF was added 2.2 mmol of tributylphosphine or triethylphosphine (in the case of **12**). The mixture was stirred 5 h at 25 °C for **7**, 2 h at 25 °C for **8**, 5 h at 40 °C for **9**, and 10 min at 25 °C for **11** and **12**.

7: ^{31}P NMR (THF) δ 30.9 (AB, ^{1}J(AB) = 444.3, PBu$_3$), −100 (AB, $^{1}J(^{31}P-^{183}W)$ = 102.5, Ph*P*W(CO)$_5$); mass spectrum (^{184}W) *m/z* 634 (M, 21%), 606 (M − CO, 27%), 578 (M − 2 CO, 23%), 550 (M − 3 CO, 60%), 522 (M − 4 CO, 55%), 494 (M − 5 CO, 42%), 404 (M − PBu$_3$ − CO, 19%), 376 (404 − CO, 36%), 348 (404 − 2 CO, 74%), 320 (404 − 3 CO, 62%), 292 (404 − 4 CO, 70%), 202 (PBu$_3$, 100%).

8: ^{31}P NMR (THF) δ 34.5 (AB, ^{1}J(AB) = 429.7, PBu$_3$), −145.1 (AB, $^{1}J(^{31}P-^{183}W)$ = 102.5, Me*P*W(CO)$_5$).

9: ^{31}P NMR (THF) δ 35.0 (AB, ^{1}J(AB) = = 439.5, PBu$_3$), −124.6 (AB, $^{1}J(^{31}P-^{183}W)$ = 102.5, allyl-*P*→W(CO)$_5$).

11: ^{31}P NMR (THF) δ 31.9 (AB, ^{1}J(AB) = 368.7, PBu$_3$), −87.2 (AB, $^{1}J(^{31}P-^{183}W)$ = 109.9, EtO$_2$CP→W(CO)$_5$); mass spectrum (^{184}W) *m/z* 630 (M, 28%), 518 (M − 4 CO, 30%), 490 (M − 5 CO, 68%), 461 (M − 6 CO − H, 100%), 262 (M − W(CO)$_5$ − CO, 99%), 234 (M − W(CO)$_5$ − CO − C$_2$H$_4$, 99%).

12: After evaporation of the solvent, the residue was chromatographed very rapidly on dry silica gel with hexane/Et$_2$O (5:1) as eluent. Data: yield 0.83 g (70%) of a yellow oil that is recrystallized in dry pentane; yellow solid; mp 62 °C; ^{31}P NMR (THF) δ 38.2 (AB, ^{1}J(AB) = 361.3, Et$_3$P), −97.4 (AB, $^{1}J(^{31}P-^{183}W)$ = 107.4, EtO$_2$C*P*→W(CO)$_5$); ^{1}H NMR (CD$_2$Cl$_2$) δ 1.18–1.35 (m, 12 H, 4 CH$_3$), 2.2 (dq, 6 H, ^{2}J(H–P) = 11.7, ^{3}J(H–H) = 7.7, ^{3}J(H–P) = 1.3, *C*H$_2$P), 4.14 (q, 2 H, ^{3}J(H–H) = 7.2, OCH$_2$); ^{13}C NMR (CD$_2$Cl$_2$) δ 7.49 (d, ^{2}J(C–P) = 4.5, CH$_3$), 14.4 (s, CH$_3$), 16.65 (dd, ^{1}J(C–P) = 39.4, ^{2}J(C–P) = 6, *C*H$_2$P), 61.47 (s, OCH$_2$), 187.67 (d, ^{1}J(C–P) = 27.3, CO$_2$), 199 (s, CO cis), 202.14 (d, ^{2}J(C–P) = 14, CO trans); IR (decalin) ν(CO) 2090 (m), 1965 (sh), 1950 (vs), 1940 (vs), 1935 (s) cm^{-1}; mass spectrum (^{184}W) *m/z* 546 (M, 40%), 518 (M − CO, 6%), 490 (M − 2 CO, 9%), 434 (M − 4 CO, 30%), 406 (M − 5 CO, 100%).

(*O*-Methyl phenylbenzylphosphinite)pentacarbonyltungsten (13). Benzaldehyde (4.2 mmol) reacts with **7** (≃4 mmol) in the presence of an excess of MeOH (50 mmol) at 25 °C for 5 min. After evaporation of the solvent, the residue was chromatographed with hexane as eluent to give **13**, yield 1.7 g (75%).

13: colorless solid, mp 80 °C; ^{31}P NMR (CDCl$_3$) δ 127.9 ($^{1}J(^{31}P-^{183}W)$ = 280.8); ^{1}H NMR (CDCl$_3$) δ 3.5 (d, ^{3}J(H–P) = 12, OCH$_3$), 3.6 (m, 2 H, *C*H$_2$P), 6.8 (m, 2 H, C$_6$H$_5$), 7.0 (m, 3 H, C$_6$H$_5$), 7.3 (m, 5 H, C$_6$H$_5$); ^{13}C NMR (CDCl$_3$) δ 46.44 (d, ^{1}J(C–P) = 22, CP), 55.14 (s, OCH$_3$), 127.0–133 (m, C$_6$H$_5$), 137.88 (d, ^{1}J(C–P) = 38.4, Cq(C$_6$H$_5$)), 196.4 (d, ^{2}J(C–P) = 7.5, CO cis), 198.73 (d, ^{2}J(C–P) = 25.7, CO trans); IR (decalin) ν(CO) 2070 (m), 1945 (vs) cm^{-1}; mass spectrum (^{184}W) *m/z* 554 (M, 30%), 526 (M − CO, 15%), 470 (M − 4 CO, 83%), 414 (M − 5 CO, 100%). Anal. Calcd for C$_{19}$H$_{15}$O$_6$PW: C, 41.18; H, 2.72. Found: C, 41.18; H, 2.57.

[*O*-Methyl phenyl[3-(2-furyl)allyl]phosphinite]pentacarbonyltungsten (14). β-(2-Furyl)acrolein (52.2 mmol) was reacted with **7** in the presence of 0.5 mmol of MeOH at 25 °C for 5 min. The final product was chromatographed with hexane/CH$_2$Cl$_2$ (4:1) as eluent; yield 0.8 g (70%).

14: Colorless solid; mp 110 °C. ^{31}P NMR (CDCl$_3$) δ 124.7 ($^{1}J(^{31}P-^{183}W)$ = 280.8); ^{1}H NMR (CDCl$_3$) δ 3.2–3.5 (m, 2 H, CH$_2$), 3.5 (d, 3 H, ^{3}J(H–P) = 12.8, OCH$_3$), 6.0 (m, 1 H, =CH), 6.2–6.5 (m, 4 H, C$_4$H$_3$O + =CH), 7.4–7.7 (m, 5 H, C$_6$H$_5$); ^{13}C NMR (CDCl$_3$) δ 42.9 (d, ^{1}J(C–P) = 23.4, CH$_2$P), 54.87 (d, ^{2}J(C–P) = 4.5, OCH$_3$), 107.9 (s, *C*H(C$_4$H$_3$O)), 111.37 (s, *C*H(C$_4$H$_3$O)), 118.8 (d, ^{3}J(C–P) = 4.9, =CH), 124 (s, ^{2}J(C–P) = 11.8, =CH), 128.85 (d, ^{3}J(C–P) = 9.3, CH(C$_6$H$_5$)), 138.12 (d, ^{1}J(C–P) = 37.4, Cq(C$_6$H$_5$)), 142.26 (s, *C*H(C$_4$H$_3$O)), 152.44 (d, ^{4}J(C–P) = 3.8, Cq(C$_4$H$_3$O)), 196.51 (d, ^{2}J(C–P) = 11.8, CO cis), 199.1 (d, ^{2}J(C–P) = 25.7, CO trans) ppm; IR (decalin) ν(CO) 2090 (m), 1950 (vs) cm^{-1}; mass spectrum (^{184}W) *m/z* 570 (M, 30%), 463 (Ph(OMe)PW(CO)$_5$, 100%). Anal. Calcd for C$_{19}$H$_{15}$O$_7$PW: C, 40.02; H, 2.65. Found: C, 39.94; H, 2.46.

(*O*-Methyl phenylisobutylphosphinite)pentacarbonyltungsten (15). Isobutyraldehyde (1.1 mmol) was reacted with **7** (1 mmol) at 25 °C for 5 min. After evaporation of the solvent, a rapid chromatography with hexane as eluent gives (phenylisobutylidenephosphine)pentacarbonyltungsten:[2] yield 0.34 g (70%); isomer ratio, *E*:*Z* = 9:1. This compound (0.7 mmol) was reacted with an excess of MeOH (10.2 mmol) in 10 mL of THF at 25 °C for 2 min. The final product **15**[2] was purified by column chromatography with hexane as eluent; yield 0.36 g (99%).

(*O*-Methyl isobutylallylphosphinite)pentacarbonyltungsten (16). Isobutyraldehyde (1.1 mmol) was reacted with **9** (≃1 mmol) in the presence of methanol (10 mmol) at 25 °C for 5 min. After evaporation of the solvent, the residue was chromatographed with hexane/Et$_2$O (95:5) as eluent; yield 0.33 g (68%).

16: yellow oil; ^{31}P NMR (CD$_2$Cl$_2$) δ 132.2 ($^{1}J(^{31}P-^{183}W)$ = 273.4); ^{1}H NMR (CD$_2$Cl$_2$) δ 1.1 (t, 6 H, CH$_3$), 1.8 (dd, 1 H, ^{2}J(H–P) = 15,

^{2}J(H–H) = 5, CH_2P), 2.0–2.4 (m, 2 H, CH_2P + CH), 3.0 (m, 2 H, CH_2P), 3.55 (d, 3 H, ^{3}J(H–P) = 12.5, OCH_3), 5.2–5.4 (m, 2 H, =CH_2), 5.7–6.0 (m. 1 H. =CH); ^{13}C NMR (CD_2Cl_2) δ 24.0 (d, ^{3}J(C–P) = 4.5, CH_3), 25.1 (d, ^{3}J(C–P) = 10.9, CH_3), 26.0 (s, CH), 42.7 (d, ^{1}J(C–P) = 22, CH_2P), 44.5 (d, ^{1}J(C–P) = 23.8, CH_2P), 53.3 (d, ^{2}J(C–P) = 27.2, OCH_3), 120.7 (d, ^{2}J(C–P) = 9.9, =CH), 129.9 (d, ^{3}J(C–P) = 4.3, =CH_2, 197.1 (d, ^{2}J(C–P) = 7.6, CO cis), 199.4 (d, ^{2}J(C–P) = 24.3, CO trans); IR (decalin) ν(CO) 2080 (m), 1950 (vs) cm^{-1}; mass spectrum (^{184}W) *m/z* 484 (M, 55%), 456 (M – CO, 23%), 428 (M – 2 CO, 23%), 400 (M – 3 CO, 89%), 372 (M – 4 CO, 66%), 344 (M – 5 CO, 59%), 299 (100%). Anal. Calcd for $C_{13}H_{17}O_6PW$: C, 32.2; H, 3.53. Found: C, 32.42; H, 3.38.

[*O*-Methyl allyl(*p*-chlorobenzyl)phosphinite]pentacarbonyltungsten (17). *p*-Chlorobenzaldehyde (3.3 mmol) was reacted with **9** ($\simeq$3.2 mmol) in the presence of MeOH (30 mmol) at 25 °C for 5 min. The final product **17** was chromatographed with hexane as eluent; yield 1.46 g (80%).

17: yellow oil; ^{31}P NMR ($CDCl_3$) δ 129.5 (^{1}J(^{31}P–^{183}W) = 278.4); ^{1}H NMR ($CDCl_3$) δ 2.7 (m, 2 H, CH_2P), 3.2 (m, 2 H, CH_2P), 3.4 (d, 3 H, ^{3}J(C–P) = 13, OCH_3), 5.1–5.3 (m, 2 H, =CH_2), 5.6–5.9 (m, 1 H, =CH), 7.0–7.3 (m. 4 H, C_6H_4); ^{13}C NMR ($CDCl_3$) δ 42.2 (d, ^{1}J(C–P) = 23.5, CH_2P), 43.5 (d, ^{1}J(C–P) = 21, CH_2P), 55.7 (s, OCH_3), 121.3 (d, ^{2}J(C–P) = 10.6, =CH), 128.9, 131.5, 132.2, 133.2 (C_6H_4 + =CH_2), 196.25 (d, ^{2}J(C–P) = 7.5. CO cis), 198.3 (d, ^{2}J(C–P) = 25.8, CO trans); IR (decalin) ν(CO) 2080 (m), 1945 (vs) cm^{-1}; mass spectrum (^{184}W) *m/z* 552 (M, 55%), 524 (M – CO, 32%), 468 (M – 3 CO, 83%), 440 (M – 4 CO, 34%), 412 (M – 5 CO, 100%). Anal. Calcd for $C_{16}H_{14}O_6PClW$: C, 34.77; H, 2.55. Found: C, 34.99; H, 2.47.

[*O*-Methyl allyl(2-thienylmethyl)phosphinite]pentacarbonyltungsten (18). Thiophene-2-carbaldehyde (4.1 mmol) was reacted with **9** ($\simeq$4 mmol) in the presence of MeOH (40 mmol) at 25 °C for 5 min. Chromatography with hexane/CH_2Cl_2 (4:1) as eluent gives **18**; yield 1.78 g (85%).

18: yellow oil; ^{31}P NMR ($CDCl_3$) δ 129.6 (^{1}J(^{31}P–^{183}W) = 278.3); ^{1}H NMR (CD_2Cl_2) δ 3.0 (m, 2 H, CH_2P), 3.6 (d, 3 H, ^{3}J(H–P) = 12.4, OCH_3), 3.6–3.8 (m, 2 H, CH_2P), 5.2–5.5 (m, 2 H, =CH_2), 5.8–6.0 (m, 1 H, =CH), 6.9–7.1 (m, 2 H, =CH(C_4H_3S)), 7.2–7.3 (m, 1 H, =CH-(C_4H_3S)); ^{13}C NMR (CD_2Cl_2) δ 38.2 (d, ^{1}J(C–P) = 22.3, CH_2P), 42.2 (d, ^{1}J(C–P) = 23.6, CH_2P), 55.8 (s, OMe), 121.5 (d, ^{2}J(C–P) = 10.5, =CH), 125.7–129.4 (m, CH(C_4H_3S) + =CH_2), 135 (d, ^{2}J(C–P) = 5.5, Cq(C_4H_3S)), 196.6 (d, ^{2}J(C–P) = 7.5, CO cis), 199 (d, ^{2}J(C–P) = 26.3, CO trans); IR (decalin) ν(CO) 1980 (m), 1945 (vs) cm^{-1}; mass spectrum (^{184}W) *m/z* 524 (M, 49%), 496 (M – CO, 83%), 440 (M – 3 CO, 77%), 412 (M – 4 CO, 72%), 384 (M – 5 CO, 30%), 343 (M – 5 CO – CH_2 – CH=CH_2, 100%). Anal. Calcd for $C_{14}H_{13}OPSW$: C, 32.08; H, 2.48. Found: C, 32.82; H, 2.34.

(2-Isopropyl-1,4,5-trimethyl-1,2,3,6-tetrahydrophosphinine)pentacarbonyltungsten (19a+b). Isobutyraldehyde (2.2 mmol) was reacted with **8** ($\simeq$2 mmol) in the presence of an excess of 2,3-dimethylbutadiene (20 mmol) at 25 °C for 15 min. After evaporation of the solvent, the final product was purified by column chromatography with hexane as eluent; yield 0.49 g (48%).

19a+b: yellow solid; mp 105 °C; ^{31}P NMR ($CDCl_3$) δ –24.0 (minor isomer), –22.7 (^{1}J(^{31}P–^{183}W) = 234.4, major isomer); ^{1}H NMR ($CDCl_3$) δ 0.8 (d, 3 H, ^{3}J(H–H) = 6.9, CH_3), 1.0 (d, 3 H, ^{3}J(H–H) = 6.8, CH_3), 1.4 (d, 3 H, ^{2}J(H–P) = 6.8, PCH_3), 1.6 (d, 6 H, CH_3), 2.0 (m, 2 H, CH_2), 2.3 (m, 1 H, CH), 2.6 (m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 12.6 (d. ^{1}J(C–P) = 23.1, PCH_3), 17.6 (s, CH_3), 20.5 (s, CH_3), 21.3 (d, ^{4}J-(C–P) = 6.4, CH_3), 22.7 (d, ^{3}J(C–P) = 14.3, CH_3), 27.7 (d, ^{2}J(C–P) = 6.3, CH), 29.85 (d, ^{2}J(C–P) = 4.2, CH_2), 38.78 (d, ^{1}J(C–P) = 15.4, CH_2P), 40.25 (d, ^{1}J(C–P) = 24.3, PCH), 121.21 (d, ^{2}J(C–P) = 7.8, =C–), 127 (d, ^{3}J(C–P) = 6.7, =C–), 197.21 (d, ^{2}J(C–P) = 7.2, CO cis), 199.64 (d, ^{2}J(C–P) = 19.9, CO trans); IR (decalin) ν(CO) 2090 (m), 1945 (vs) cm^{-1}; mass spectrum (^{184}W) *m/z* 508 (M, 61%), 480 (M – CO, 19%), 452 (M – 2 CO, 100%), 424 (M – 4 CO, 47%). Anal. Calcd for $C_{16}H_{21}O_5PW$: C, 37.82; H, 4.16. Found: C, 37.84; H, 4.13.

[2-(*p*-Chlorophenyl)-1,4,5-trimethyl-1,2,3,6-tetrahydrophosphinine]-pentacarbonyltungsten (20a+b). *p*-Chlorobenzaldehyde (2.2 mmol) was reacted with **8** ($\simeq$2 mmol) in the presence of an excess of 2,3-dimethylbutadiene (20 mmol) at 25 °C for 15 min. Chromatography of the crude mixture with hexane as eluent gives **20a+b**, yield 0.43 g (37%).

20a+b: yellow solid; mp 126 °C; ^{31}P NMR ($CDCl_3$) δ –18.0 (minor isomer, 30%), –25.0 (^{1}J(^{31}P–^{183}W) = 229.5) (major isomer, 70%); ^{1}H NMR ($CDCl_3$) δ 1.4 (d, 3 H, ^{2}J(H–P) = 6.7, CH_3P), 1.6 (s, CH_3), 1.7 (s, CH_3), 2.2–2.7 (m, 4 H, CH_2), 3.0 (m, 1 H, CH), 6.9–7.3 (m, 4 H, C_6H_4); ^{13}C NMR ($CDCl_3$) δ 13.52 (d, ^{1}J(C–P) = 23.6), 20.1 (s, CH_3), 21.55 (d, ^{3}J(C–P) = 7.2), 35.87 (s, CH_2), 36.57 (d, ^{1}J(C–P) = 18.1, CH_2P), 42.1 (d, ^{1}J(C–P) = 22, CHP), 121.63 (d, ^{3}J(C–P) = 6.9, =C–), 127.35 (d, ^{2}J(C–P) = 8.2, =C–), 129–139 (m, C_6H_4), 196.67 (d, ^{2}J(C–P) = 7.1, CO cis), 199.16 (d, ^{2}J(C–P) = 21.22, CO trans); IR (decalin) ν(CO) 2090 (m), 1940 (vs) cm^{-1}; mass spectrum (^{184}W) *m/z* 577 (M, 25%), 549 (M – CO, 9%), 491 (M – 4 CO – 2 H, 100%). Anal. Calcd for $C_{19}H_{18}PClW$: C, 39.57; H, 3.14. Found: C, 39.74; H, 3.04.

(*O*-Benzoyl phenylbenzylphosphinite)pentacarbonyltungsten (21). Benzaldehyde (2.2 mmol) was reacted with **7** (2 mmol) in the presence of benzoic acid (2.2 mmol) at 25 °C for 5 min. After evaporation of the solvent, the mixture was chromatographed with hexane/CH_2Cl_2 (3:1) as eluent; yield 1.1 g (80%).

21: colorless solid; mp 172 °C; ^{31}P NMR ($CDCl_3$) δ 123.4 (^{1}J(^{31}P–^{183}W) = 284.2; ^{1}H NMR ($CDCl_3$) δ 3.8 (d, ^{1}J(H–H) = 14.1, H), 4.3 (q, ^{1}J(H–H) = 14.1, ^{2}J(H–P) = 9.3, H), 6.7–8.2 (m, 15 H, 3 C_6H_5); ^{13}C NMR ($CDCl_3$) δ 47.11 (d, ^{1}J(C–P) = 13.3, CH_2), 127.2–136.1 (m, C_6H_5), 164.76 (d, ^{2}J(C–P) = 4.3, CO), 196.0 (d, ^{2}J(C–P) = 7.5, CO cis), 198.74 (d, ^{2}J(C–P) = 29.6, CO trans); IR (decalin) ν(CO) 2085 (m), 1960 (vs), 1950 (s) cm^{-1}; mass spectrum (^{184}W) *m/z* 616 (M – CO, 23%), 588 (M – 2 CO, 6%), 560 (M – 3 CO, 19%), 532 (M – 4 CO, 4%), 504 (M – 5 CO – H, 100%). Anal. Calcd for $C_{25}H_{17}O_7PW$: C, 46.61; H, 2.65. Found: C, 46.61; H, 2.6.

X-ray Structure Determination for 12. Crystals of **12**, $C_{14}H_{20}O_7P_2W$, were grown at –18 °C from a pentane solution of the compound. Data were collected at 18 ± 1 °C on an Enraf-Nonius CAD4 diffractometer. The crystal structure was solved and refined with the Enraf-Nonius-supplied SDP package. The compound crystallizes in space group $P1$, a = 7.233 (1) Å, b = 10.137 (1) Å, c = 14.878 (1) Å, α = 104.43 (1)°, β = 90.26 (1)°, γ = 106.88 (1)°, V = 1007.40 (42) Å^3, Z = 2, d_{calc} = 1.800 g/cm^3, Mo Kα radiation (λ = 0.71073 Å), graphite monochromator, μ = 60.4 cm^{-1}, $F(000)$ = 528. A total of 3538 unique reflections were recorded in the range $2° \leq 2\theta \leq 50.0°$ of which 360 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 3178 for solution and refinement. The structure was solved by Patterson methods, yielding a solution for the tungsten and two phosphorus atoms. The hdrogen atoms were included as fixed contribution in the final stages of least-squares refinement while anisotropic temperature factors were used for all other atoms. A non-Poisson weighting scheme was applied with a p = 0.05. The final R factors were R = 0.023, R_w = 0.032, GOF = 1.09.

Supplementary Material Available: Tables of experimental data, bond distances, bond angles, positional parameters, and refined displacement parameter expressions (5 pages); listing of calculated and observed structure factors (17 pages). Ordering information is given on any current masthead page.