(M, 6), 630 (M – CO, 17), 602 (M – 2CO, 18), 574 (M – 3CO, 16), 518 (M – "5CO", 28), 490 (M – "6CO", 40), 462 (M – "7CO", 28), 434 (M – "8CO", 41), 378 (M – Fe – 8CO, 100).

X-ray Structure Determination for 15. Crystals of **15**, $C_{16}H_{15}O_8PFeW$, were grown at −18 °C from an ether 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 by using the Enraf-Nonius supplied SDP package. The compound crystallizes in space group $P2_1/c$, a = 10.220 (1) Å, b = 12.705 (1) Å, c = 15.914 (1) Å, β = 90.79 (1)°, V = 2066.10 (49) Å^3, Z = 4, d_{calc} = 1.946 g/cm^3; Mo Kα radiation (λ = 0.710 73 Å), graphite monochromator, μ = 65.0 cm^{-1}, $F(000)$ = 1156. A total of 6539 unique reflexions were recorded in the range $2° \leq 2\theta \leq 60.0°$ of which 2149 were considered as unobserved ($F^2 < 3\sigma(F^2)$), leaving 4390 for solution and refinement. The structure was solved by Patterson methods, yielding a solution for the tungsten and iron atoms. The hydrogen atoms were included as a 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 factor equal to 0.08. The final R factors were R = 0.029, R_ω = 0.052, GOF = 1.10. Selected bond distances and angles are given in the caption for Figure 1.

Supplementary Material Available: Experimental details for crystal structure determination and listings of bond lengths, bond angles, and refined displacement parameters for **15** (4 pages); a listing of observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

The "Phospha-Wittig" Reaction: A New Method for Building Phosphorus–Carbon Double and Single Bonds from Carbonyl Compounds

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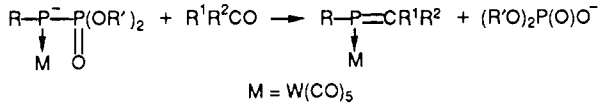
The so-called "phospha-Wittig" reagents $[(EtO)_2P(O)PHR]M(CO)_5$ (M = Mo, W) are obtained via the reaction of primary phosphine complexes $(RPH_2)M(CO)_5$ with lithium diisopropylamide and diethyl chlorophosphate. The corresponding anions $[(EtO)_2P(O)—P^-R]M(CO)_5$ react with carbonyl compounds under mild conditions to give the phosphaalkene complexes $[R^1R^2C{=}PR]M(CO)_5$. A study of this reaction with R = Ph, R^1 = *i*-Pr, and R^2 = H has shown that the kinetic product is the (*Z*)-phosphaalkene complex, whereas the thermodynamic product is the *E* isomer. The stereochemistry of these complexes was established by X-ray crystal structure analysis. With α-diketones, only one carbonyl bond is converted into a P=C double bond, probably for steric reasons. Most of the phosphaalkene complexes thus obtained easily react with methanol or 2,3-dimethylbutadiene. The phosphane–$Mo(CO)_5$ complexes synthesized via such a scheme are easily transformed into the corresponding *P*-sulfides by simple heating with sulfur in toluene. Thus, the "phospha-Wittig" reaction can also be viewed as a new tool for building organophosphorus species with P—C single bonds.

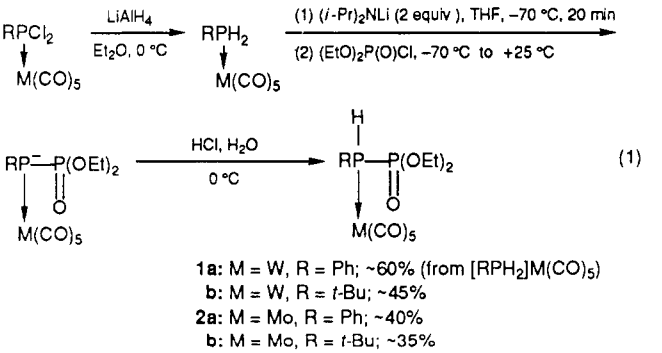
In a preliminary note,[1] we have shown that it is possible to devise a phosphorus equivalent for the Wittig–Horner synthesis of olefins. In this so-called "phospha-Wittig" process, a carbonyl compound is transformed into a phosphaalkene complex:



This method has a wide applicability and can serve as an original route to both PC double and single bonds. In the work that is described hereafter, we will report on an alternate and more convenient synthesis of the starting reagents, provide a further demonstration of the generality of this "phospha-Wittig" reaction, and depict a technique for removing the metal from the final organophosphorus products.

Results and Discussion

In our previous work, the starting secondary phosphorylphosphine complexes **1** were prepared via the nucleophilic attack of $(EtO)_2PO^-$ onto (phosphirane)pentacarbonyltungsten complexes.[2] We have devised a new simpler approach, which is depicted in eq 1. This approach works with tungsten and molybdenum carbonyl complexes as well. In contrast, the free secondary phosphorylphosphines are unstable[3] and no clean "phospha-



1a: M = W, R = Ph; ~60% (from $[RPH_2]M(CO)_5$)
b: M = W, R = *t*-Bu; ~45%
2a: M = Mo, R = Ph; ~40%
b: M = Mo, R = *t*-Bu; ~35%

(1) Marinetti, A.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1382.

(2) Marinetti, A.; Mathey, F. *Tetrahedron* **1989**, *45*, 3061.

(3) See, however, the work of Schmidpeter, who characterized the phosphorylphosphido anion $PhP^-P(O)Ph_2$: Schmidpeter, A. *Nova Acta Leopold* **1985**, *59*, 69. The corresponding secondary phosphorylphosphine appears to be unstable as in our case.

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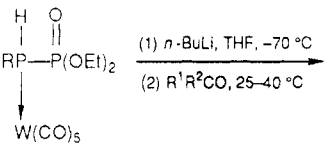
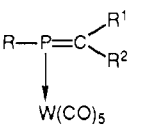
Wittig" reaction can be carried out with them.

The phosphaalkene complexes obtained from these "phospha-Wittig" reagents and ketones are generally reasonably stable and can be isolated in the pure state after a rapid chromatographic workup. Several new examples are listed in eq 2 and 3. From these examples, it clearly

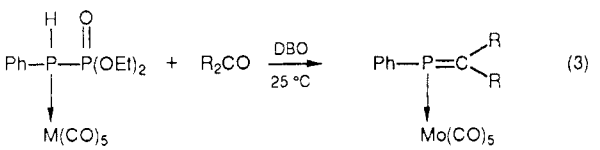


1a: R = Ph
b: R = *t*-Bu
c: R = Me



(2)

3: R = Ph, R^1 = Et, R^2 = Me; 37% (2 isomers)
4: R = Ph, R^1–C–R^2 = 2-adamantylidene; 66%
5: R = Me, R^1–C–R^2 = 2-adamantylidene; 62%
6: R = *t*-Bu, R^1 = R^2 = Me; 58%

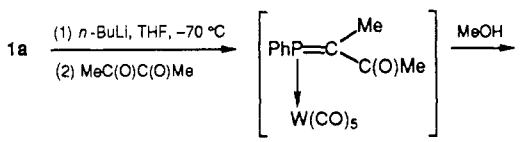


(3)

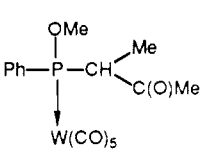
2a

7: R = Me, 56%
8: R–R = $-(CH_2)_4-$, 37%

appears that the overall yields of phosphaalkene complexes increase with the steric bulk of the substituents either at phosphorus or at carbon. This does not mean that the reaction works better in such cases but that the loss of product is minimized during the purification procedure. In particular, the addition of water onto the P=C double bond proceeds slower when the bond is sterically hindered. On the other hand, an excess of steric hindrance may block the condensation between the ketone and the "phospha-Wittig" reagent. Indeed, we have already observed that the anion from **1a** is unable to react with benzophenone.[1] This observation explains why a "phospha-Wittig" reagent such as **1a** is only able to substitute one of the two keto groups of α-diketones (eq 4). The keto-substituted phosphaalkene complex **9** thus obtained is so reactive that we have been obliged to characterize it as its methanol adduct **10** (eq 4).



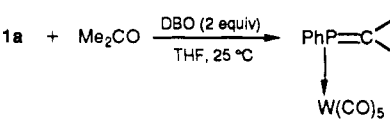
9



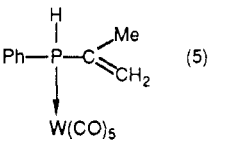
(4)

10 (80%, 2 isomers)

While using DBO (1,4-diazabicyclo[2.2.2]octane) as a base for removing the proton from **1a**, we discovered that an excess of DBO could catalyze the slow conversion of a phosphaalkene complex such as **11**[1] into its secondary vinylphosphine isomer **12** at room temperature (eq 5). The conversion was easily monitored by ^{31}P NMR spectroscopy. The ^{31}P resonance of **11** at low field ($\delta^{31}P$(**11**) = +176 ppm) slowly disappeared and was replaced by a new resonance at high field showing a characteristic ^1J(P–H) coupling ($\delta^{31}P$(**12**) = –6.4 ppm, ^1J(P–H) = 344 Hz). Apparently, the P=C double bond renders the methyl α-hydrogens of **11** sufficiently acidic. Thus, DBO is able to abstract a proton from **11** to generate a delocalized phosphaallyl anion that is protonated at phosphorus (eq 6). It is interesting to compare this result with the reverse

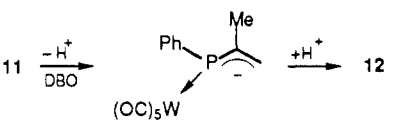


11



(5)

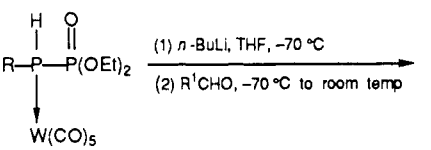
12



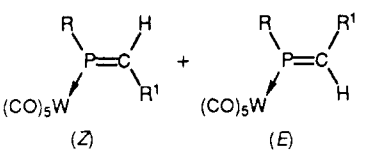
(6)

conversion of a free secondary vinylphosphine into the corresponding phosphaalkene via a formal hydrogen 1,3-shift in a neutral medium.[4] It is now clear that a close parallelism can be drawn between allyl and phosphaallyl chemistry. This parallelism is completed by the recent discovery of a series of stable η^3-phosphaallyl complexes.[5]

In contrast to what occurs with ketones, the phosphaalkene complexes obtained from aldehydes and "phospha-Wittig" reagents are normally unstable and highly reactive. In order to get stable compounds, it is necessary to use bulky substituents as depicted in eq 7.



1



(*Z*) (*E*)

(7)

13(*Z*) + **13**(*E*):R = Ph, R^1 = Me_2CH; 70% (isomer ratio 1:2)
14(*Z*): R = Me_3C, R^1 = Me_2CH; 54%
15(*Z*) + **15**(*E*):R = Ph, R^1 = Me_3C; 68% (isomer ratio 9:1)
16(*Z*): R = Me_3C, R^1 = Me_3C; 87%
17: R = Me_3C, R^1 = 4-Cl-Ph; ($\delta^{31}P$ = +251 ppm)
R = Me_3C, R^1 = 2-thienyl; ($\delta^{31}P$ = +225 ppm)

When isobutyraldehyde is added to the anion of **1a** at room temperature, **13**(*Z*) is almost the only isomer formed. When the addition is performed at −70 °C, **13**(*Z*) and **13**(*E*) are both obtained in a 1:2 ratio. The most significant NMR characteristics of **13**(*Z*) and **13**(*E*) are given as follows: **13**(*Z*), $\delta_{^{31}P}$ = +190 ppm, $\delta_{^{13}C=P}$ = 180.7 ppm (^1J(C–P)

(4) Mercier, F.; Hugel-Le Goff, C.; Mathey, F. *Tetrahedron Lett.* **1989**, *30*, 2397.

(5) Mercier, F.; Fischer, J.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 357. Mercier, F.; Hugel-Le Goff, C.; Mathey, F. *Organometallics* **1988**, *7*, 955. Hugel-Le Goff, C.; Mercier, F.; Ricard, L.; Mathey, F. *J. Organomet. Chem.* **1989**, *363*, 325.

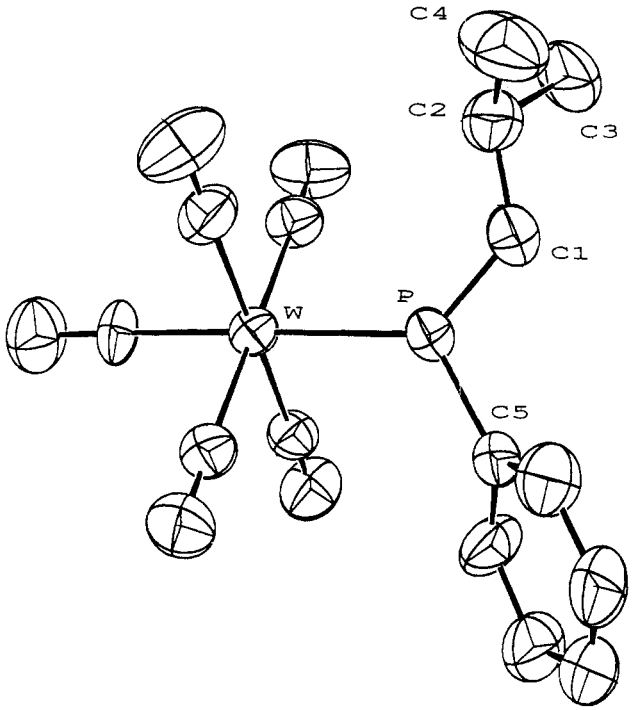


Figure 1. ORTEP drawing of one molecule of **13**(*Z*). Vibrational ellipsoids are scaled to enclose 40% of the electron density. Hydrogen atoms are omitted for clarity. Principal bond distances (Å): P–C_1 = 1.64 (1); P–C_5 = 1.801 (9); P–W = 2.467 (2). Selected bond angles (deg): W–P–C_1 = 131.4 (3); W–P–C_5 = 122.9 (3); C_1–P–C_5 = 105.5; P–C_1–C_2 = 126.2 (8).

= 44.8 Hz), $\delta_{=CH}$ = 7.82 ppm (^2J(H–P) = 19.2 Hz); **13**(*E*), $\delta_{^{31}P}$ = +185 ppm, $\delta_{^{13}C=P}$ = 180.4 ppm (^1J(C–P) = 40.6 Hz), $\delta_{=CH}$ = 7.29 ppm ^2J(H–P) = 18.8 Hz). According to Yoshifuji,[6] a complex of (*Z*)-phosphaalkene shows a more shielded phosphorus and =CH proton than the complex of the corresponding (*E*)-phosphaalkene. Thus, Ph and *i*-Pr substituents would be trans in the thermodynamic isomer **13**(*Z*) and cis in the kinetic isomer **13**(*E*). However, we felt that these NMR assignments were not reliable enough and we carried out the X-ray crystal structure analysis of **13**(*Z*) in order to confirm its stereochemistry. The most significant structural features of **13**(*Z*) are collected in the caption of Figure 1. The trans stereochemistry of **13**(*Z*) is thus unambiguously established.

When isobutyraldehyde is added to the anion of the more bulky **1b**, only one isomer of **14** is formed. Since there was no possibility of establishing the stereochemistry of **14** on the basis of NMR data, we also carried out the X-ray crystal structure analysis of **14**. The most significant structural features of **14** are given in the caption of Figure 2. The trans stereochemistry of **13**(*Z*) and **14** clearly demonstrate that the thermodynamic preference is governed by the steric bulk of the phosphaalkene substituents. It may seem surprising that the complexation has no influence on the stereochemistry of the P=C double bond. Using the geometry of **14** and the calculated geometry of the corresponding cis isomer obtained via a 180° rotation of the *C*(H)CH Me_2 isobutylidene group around the P=C double bond, we found that the *W*···CHMe_2 distance in **14** is 4.04 Å, whereas the Me_3C···CHMe_2 distance in the corresponding cis isomer is only 3.13 Å. Thus, clearly, the P substituent has more steric influence than the P-complexing group on the stereochemistry of the P=C double bond. From another standpoint, the kinetic preference for

(6) Yoshifuji, M.; Toyota, K.; Inamoto, N. *Tetrahedron Lett.* **1985**, *26*, 1727.

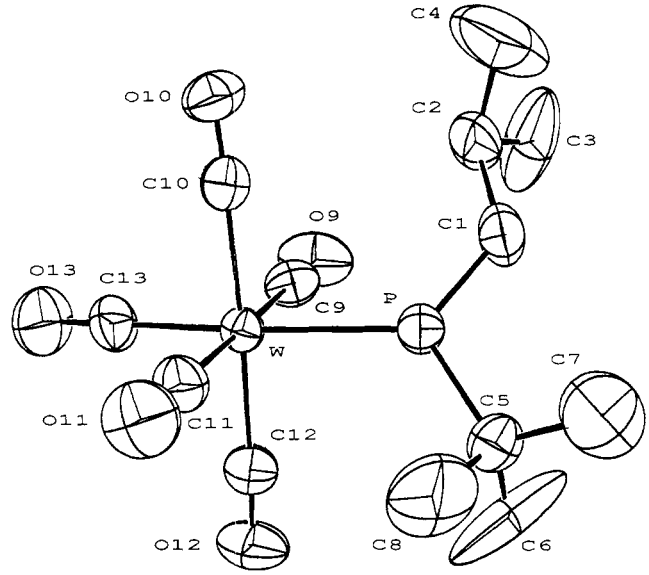
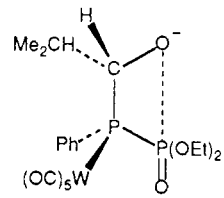


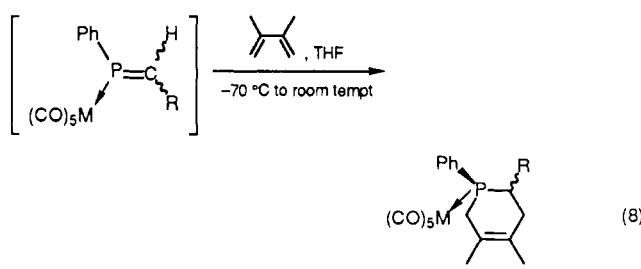
Figure 2. ORTEP drawing of one molecule of **14**. Vibrational ellipsoids are scaled to enclose 40% of the electron density. Hydrogen atoms are omitted for clarity. Principal bond distances (Å): P–C_1 = 1.65 (1); P–C_5 = 1.861 (9); P–W = 2.490 (2); W–C_9 to W–C_{12} = 2.02 (1)–2.054 (9); W–C_{13} = 1.97 (1). Selected bond angles (deg): W–P–C_1 = 125.7 (4); W–P–C_5 = 125.9 (3); C_1–P–C_5 = 108.4 (5); P–C_1–C_2 = 125.7 (7); P–W–C_9 to P–W–C_{12} = 87.7 (3)–93.4 (3); P–W–C_{13} = 175.9 (3).

the more hindered phosphaalkene complex **13**(*E*) can be explained by the preferential formation and decomposition of the intermediate **19** at low temperature.



19

As expected, stable phosphaalkene complexes **15** and **16** are also obtained from the more bulky pivalaldehyde. In the first case (**15**, R = Ph), the ^{31}P NMR spectrum of the crude reaction mixture also showed the presence of a small amount of the *E* isomer (ratio *Z*/*E* ca. 9:1). In contrast, when less hindered aldehydes such as *p*-chlorobenzaldehyde and 2-formylthiophene are used, the resulting phosphaalkene complexes (**17**, **18**) are so unstable that their formation can only be monitored by ^{31}P NMR spectroscopy or by trapping reactions (eq 8). Only one isomer each of **20** and **21** was obtained in the pure state, but the stereochemistry was not unambiguously established.

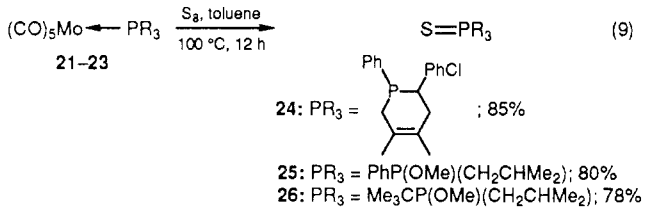


(8)

20: M = W, R = 2-thienyl; 39%
21: M = Mo, R = 4-Cl-Ph; 61%

Most, if not all, of the P=C double bonds prepared via the "phospha-Wittig" approach would be unstable in the free uncomplexed state. It must be recalled here that the

simplest stable phosphaalkene with only hydrocarbon substituents is 1-mesityl-2,2-diphenylphosphaethylene,[7] which is plagued by a somewhat reduced reactivity in cycloaddition reactions.[8] Our final aim in the development of this "phospha-Wittig" reaction was to get a ready access to P=C double bonds with "ordinary" substituents such as Ph, Me, Et, etc. and to use them as synthetic tools to build more sophisticated organophosphorus species via classical addition or cycloaddition reactions. In order to complete such a synthetic scheme, it was obviously necessary to devise a simple method for removing the complexing group from the final products. A technique for breaking the P—W bond in P–W(CO)$_5$ complexes has already been developed in our laboratory,[9] but it is rather cumbersome and we have looked for a simpler method. Following an earlier work,[10] we have found that the P–Mo(CO)$_5$ complexes are easily transformed into the corresponding *P*-sulfides by simple heating with sulfur in toluene solution. Three examples illustrate this point (eq 9). Complexes **21**, **22**, and **23** are obtained by the addition



of methanol or 2,3-dimethylbutadiene to phosphaalkene–Mo(CO)$_5$ complexes (see Experimental Section and ref 1). Thanks to this mild decomplexation technique, the "phospha-Wittig" reaction can now be viewed as a new versatile method for building organophosphorus species containing P—C single bonds.

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. Chemical 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 the (RPH$_2$)M(CO)$_5$ Complexes (R = Ph, *t*-Bu, Me; M = W, Mo). (a) To a stirred suspension of 50 mmol of M(CO)$_6$ in 200 mL of CH_3CN was added 50 mmol of $Me_3NO\cdot 2H_2O$, in small portions, over 30 min. The yellow solution was stirred for a further 30 min and then evaporated to dryness in vacuo. The residue was dissolved in dry toluene and the solution evaporated to dryness. The crude M(CO)$_5$(CH_3CN) was dissolved in 50 mL of THF, 50 mmol of dichlorophosphine (RPCl$_2$) was added, and the mixture was heated at 50 °C overnight. After evaporation of the solvent, addition of hexane and filtration of the solution give the (RPCl$_2$)M(CO)$_5$ complexes.

(b) To a stirred solution of 50 mmol of $LiAlH_4$ (Aldrich pellets, 10 × 13 mm) in ether at 0 °C was added an ethereal solution of the crude (RPCl$_2$)M(CO)$_5$ complex. The mixture was warmed to room temperature and then hydrolyzed at 0 °C with water. After extraction with ether and evaporation, the residue was chromatographed on a silica gel column with hexane as eluent. (RPH$_2$)M(CO)$_5$ complexes were obtained with an overall yield of about 50–60%.

Synthesis of the Phosphorylphosphine Complexes (1a,b, 2a,b). To a solution of 40 mmol of lithium diisopropylamide (LDA) in THF at −78 °C was added a THF solution of 20 mmol of the (RPH$_2$)M(CO)$_5$ complex. After 20 min, diethyl chlorophosphate (25 mmol) was added at −78 °C. The mixture was warmed to 0 °C and hydrolyzed with aqueous hydrochloric acid (pH < 7). After evaporation and extraction with ether, the crude product was purified by column chromatography (hexane–ether, 70:30). **1a**: yield 60%.[2] **1b**: yield 45%; colorless solid; mp 72 °C; ^{31}P NMR (ether) δ 22.5 (*AB*, $^1J_{AB}$ = 51.3, P(O)(OEt)$_2$), −20.2 (*AB*, $^1J(^{183}W-^{31}P)$ = 219.7); ^{1}H NMR (C_6D_6): δ 0.97 (t, CH_2CH_3), 0.99 (t, CH_2CH_3), 1.18 (d, ^3J(H–P) = 16.7, CMe_3), 3.9 (m, 4 H, CH_2CH_3), 4.41 (d, ^1J(H–P) = 320.9, PH); IR (decalin) ν(CO) 2070 (m), 1950 (s), 1940 (vs) cm^{-1}; mass spectrum (^{184}W) *m/z* (relative intensity) 550 (M, 13), 438 (M − 5CO, 100). Anal. Calcd for $C_{13}H_{20}O_8P_2W$: C, 28.38; H, 3.66. Found: C, 28.36; H, 3.59. **2a**: yield 40% (note: for molybdenum complexes, the reaction mixture must be hydrolyzed by adding the reaction solution *to* the aqueous hydrochloric acid at 0 °C); colorless solid; mp <50 °C; ^{31}P NMR (CH_2Cl_2) δ 22.7 (*AB*, $^1J_{AB}$ = 58.6, P(O)(OEt)$_2$), −33.4 (*AB*); ^{1}H NMR (C_6D_6) δ 0.92 (t, CH_2CH_3), 0.94 (t, CH_2CH_3), 3.8 (m, 4 H, CH_2CH_3), 5.34 (dd, ^1J(H–P) = 328.7, ^2J(H–P) = 1.9, PH); IR (decalin) ν(CO) 2070 (m), 1960 (vs) cm^{-1}; mass spectrum (^{98}Mo) *m/z* 484 (M, 11), 344 (M − 5CO, 80). Anal. Calcd for $C_{15}H_{16}O_8P_2Mo$: C, 37.34; H, 3.35. Found: C, 37.54; H, 3.47. **2b**: yield 35%; colorless solid; mp <50 °C; ^{31}P NMR (CH_2Cl_2): δ 25.4 (*AB*, $^1J_{AB}$ = 22.0, P(O)(OEt)$_2$), −2.1 (*AB*); ^{1}H NMR (C_6D_6) δ 0.99 (t, CH_2CH_3), 1.01 (t, CH_2CH_3), 1.19 (d, ^3J(H–P) = 16.4, CMe_3), 3.8 (m, 4 H, CH_2CH_3), 4.09 (d, ^1J(H–P) = 308.4, PH); IR (decalin) ν(CO) 2075 (m), 1950 (vs) cm^{-1}; mass spectrum (^{98}Mo) *m/z* 462 (M, 11), 351 (M − 4CO, 100). Anal. Calcd for $C_{13}H_{20}O_8P_2Mo$: C, 33.75; H, 4.36. Found: C, 33.96; H, 4.41.

Synthesis of the Phosphaalkene Complexes. Method A. A solution of the phosphorylphosphine complex (**1a–c**) (1 mmol) in THF was cooled to −78 °C. *n*-BuLi (0.7 mL, 1.6 M solution in hexane) was then added. After a few minutes, 1 mmol or an excess of the appropriate carbonyl compound was added. The reaction mixture was then warmed to room temperature and the reaction was monitored by ^{31}P NMR spectroscopy. In the case of less reactive carbonyl compounds, the reaction mixture can be heated at 40 °C to perform the phosphaalkene synthesis. Higher temperatures must be avoided owing to a transformation of the phosphorylphosphine anion itself. When the reaction was completed, THF was partly evaporated, pentane was added, and the solution was directly chromatographed on a silica gel column (pentane). The lithium salts of the phosphorylphosphine complexes **1a–c** and **2a,b** are characterized by their ^{31}P NMR spectra in THF at room temperature. **1a** (lithium salt): ^{31}P NMR δ 62.7 (*AB*, $^1J_{AB}$ = 383.3), −107.5 (*AB*, $^1J(^{31}P-^{183}W)$ = 97.7). **1b** (lithium salt): ^{31}P NMR δ 65.4 (*AB*, $^1J_{AB}$ = 429.7), −75.4 (*AB*). **1c** (lithium salt): ^{31}P NMR δ 69.2 (*AB*, $^1J_{AB}$ = 402.8), −155.3 (*AB*, $^1J(^{31}P-^{183}W)$ = 90.3). **2a** (lithium salt): ^{31}P NMR δ 65.1 (*AB*, $^1J_{AB}$ = 393.1), −94.96 (*AB*). **2b** (lithium salt): ^{31}P NMR δ 68.5 (*AB*, $^1J_{AB}$ = 449.2), −63.42 (*AB*).

[Phenyl(1-methylpropylidene)phosphine]pentacarbonyltungsten (3). A 5-mmol amount of 2-butanone was reacted with the phosphorylphosphine anion **1a** at 40 °C for 2.5 h. **3**: yield 0.18 g (37%); isomer ratio 1:1, yellow oil; ^{31}P NMR (C_6D_6) δ 169.8 ($^1J(^{183}W-^{31}P)$ = 255.4), 169.6 ($^1J(^{183}W-^{31}P)$ = 254.9); ^{1}H NMR (C_6D_6) δ 0.57 (t, CH_2CH_3), 0.94 (t, CH_2CH_3), 1.58 (d, ^3J(H–P) = 24.9, CH_3), 1.96 (d, ^3J(H–P) = 31.6, CH_3), 1.94 (dq, ^3J(H–P) = 20.1, CH_2), 2.42 (dq, ^3J(H–P) = 27.0, CH_2); ^{13}C NMR (C_6D_6) δ 14.19 (d, ^3J(C–P) = 16.2, CH_2CH_3), 14.53 (d, ^3J(C–P) = 17.7, CH_2CH_3), 23.19 (d, ^2J(C–P) = 19.8, C–CH_3), 23.28 (d, ^2J(C–P) = 9.9, CCH_3), 32.76 (d, ^2J(C–P) = 9.1, CCH_2), 33.27 (d,

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^2J(C–P) = 20.3, CCH_2), 190.39 (d, ^1J(C–P) = 30.7, P=*C*), 191.21 (d, ^1J(C–P) = 30.2, P=*C*), 195.62 (d, ^2J(C–P) = 10.1, cis CO), 199.78 (d, ^2J(C–P) = 28.7, trans CO); IR (decalin) ν(CO) 2075 (m), 1950 (vs) cm^{-1}; mass spectrum (^{184}W) *m/z* 488 (M, 40), 348 (M – 5CO, 100).

(Phenyl-2-adamantylidenephosphine)pentacarbonyltungsten (4). A 1.1-mmol amount of 2-adamantanone was reacted with the anion derived from **1a** at 40 °C for 6 h. **4**: yield 0.37 g (66%); yellow solid; mp 128 °C (pentane); ^{31}P NMR (C_6D_6) δ 139.7 ($^1J(^{183}W-^{31}P)$ = 253.9 Hz); ^{1}H NMR (C_6D_6) δ 3.02 (m, ^3J(H–P) = 8.9, CC*H*), 3.36 (m, ^3J(H–P) = 17.5, CC*H*); ^{13}C NMR (C_6D_6) δ 201.86 (d, ^1J(C–P) = 36.2, P=*C*); IR (decalin) ν(CO) 2070 (m), 1950 (vs) cm^{-1}; mass spectrum (^{184}W) *m/z* 566 (M, 60), 510 (M – 2CO, 100).

(Methyl-2-adamantylidenephosphine)pentacarbonyltungsten (5). 2-Adamantanone (1.1 mmol) was reacted with the anion of **1c** between −70 and +25 °C. **5**: yield 0.31 g (62%); yellow solid; mp 125 °C; ^{31}P NMR (C_6D_6) δ 126.6 ($^1J(^{183}W-^{31}P)$ = 251.5); ^{1}H NMR (C_6D_6) δ 1.37 (d, ^2J(H–P) = 12.4, PCH_3), 2.89 (m, ^3J(H–P) = 8.3, CC*H*), 3.15 (m, ^3J(H–P) = 16.9, CC*H*); ^{13}C NMR (C_6D_6) δ 15.26 (d, ^1J(C–P) = 7.0, PCH_3), 198.71 (d, ^1J(C–P) = 39.3, P=*C*); IR (decalin) ν(CO) 2075 (m), 1950 (vs) cm^{-1}; mass spectrum (^{184}W) *m/z* 504 (M, 66), 364 (M – 5CO, 100). Anal. Calcd for $C_{16}H_{17}O_5PW$: C, 38.12; H, 3.40. Found: C, 37.97; H, 3.39.

(*tert*-Butylisopropylidenephosphine)pentacarbonyltungsten (6). Acetone (5 mmol) was reacted with the anion of **1b** at 40 °C for 2.5 h. **6**: yield 0.26 g (58%); yellow solid; mp 151 °C (pentane); ^{31}P NMR (C_6D_6) δ 212.6 ($^1J(^{183}W-^{31}P)$ = 241.7); ^{1}H NMR (C_6D_6) δ 1.07 (d, ^3J(H–P) = 14.1, CMe_3), 1.75 (d, ^3J(H–P) = 22.3, CCH_3), 1.97 (d, ^3J(H–P) = 29.8, CCH_3); ^{13}C NMR (C_6D_6) δ 27.71 (d, ^2J(C–P) = 13.1, CCH_3), 30.88 (d, ^2J(C–P) = 2.5, CMe_3), 31.72 (d, ^2J(C–P) = 15.1, CCH_3), 38.49 (s, *C*Me$_3$), 183.50 (d, ^1J(C–P) = 31.7, P=*C*); IR (decalin) ν(CO) 2075 (m), 1945 (vs) cm^{-1}; mass spectrum (^{184}W) *m/z* 454 (M, 45), 314 (M – 5CO, 100). Anal. Calcd for $C_{12}H_{15}O_5PW$: C, 31.74; H, 3.33. Found: C, 31.86; H, 3.12.

(Phenylisobutylidenephosphine)pentacarbonyltungsten (13(*Z*),(*E*)). Isobutyraldehyde (1.1 mmol) reacts with the anion of **1a** between −70 °C and room temperature: yield 0.34 g (70%); isomer ratio (13(*Z*):13(*E*)) 1:2. When isobutyraldehyde was added to the same anion at room temperature, an exothermic reaction was observed and the isomer ratio thus obtained was (13(*Z*):13(*E*)) 9:1. **13(*Z*)**: yellow solid; mp 85 °C (pentane); ^{31}P NMR (C_6D_6) δ 189.1 ($^1J(^{183}W-^{31}P)$ = 258.8); ^{1}H NMR (C_6D_6) δ 0.97 (dd, ^3J(H–H) = 6.5, ^3J(H–P) = 1.3, CHMe_2), 3.0 (m, C*H*Me$_2$), 7.82 (dd, ^2J(C–P) = 19.2, ^3J(H–H) = 11.8, P=CH); ^{13}C NMR (C_6D_6) δ 23.94 (d, ^3J(C–P) = 17.1, CHMe_2), 34.14 (d, ^2J(C–P) = 9.1, *C*HMe$_2$), 180.68 (d, ^1J(C–P) = 44.8, P=CH), 195.09 (d, ^2J(C–P) = 9.6, cis CO), 198.82 (d, ^2J(C–P) = 28.7, trans CO); IR (decalin) ν(CO) 2070 (m), 1955 (vs) cm^{-1}. **13(*E*)** (mixture with **13(*Z*)**): ^{31}P NMR (C_6D_6) δ 183.9 ($^1J(^{183}W-^{31}P)$ = 258.8); ^{1}H NMR (C_6D_6) δ 0.67 (dd, ^3J(H–H) = 6.5, ^3J(H–P) = 1.1, CHMe_2), 2.6 (m, C*H*Me$_2$), 7.29 (dd, ^2J(H–P) = 18.8, ^3J(H–H) = 11.0, P=CH); ^{13}C NMR (C_6D_6) δ 23.70 (d, ^3J(C–P) = 16.0, CHMe_2), 34.58 (d, ^2J(C–P) = 15.8, *C*HMe$_2$), 180.39 (d, ^1J(C–P) = 40.3, P=CH), 195.48 (d, ^2J(C–P) = 9.6, cis CO); mass spectrum (^{184}W) *m/z* 488 (M, 21), 348 (M – 5CO, 100). Anal. Calcd for $C_{15}H_{13}O_5PW$: C, 36.91; H, 2.68. Found: C, 37.19; H, 2.84.

(*tert*-Butylisobutylidenephosphine)pentacarbonyltungsten (14). Isobutyraldehyde (3 mmol) reacts with the anion of **1b** between −70 and +25 °C. **14**: yield 0.25 g (54%); yellow solid; mp 72 °C (pentane); ^{31}P NMR (C_6D_6) δ 233.8 ($^1J(^{183}W-^{31}P)$ = 244.1); ^{13}C NMR (C_6D_6) δ 23.91 (d, ^3J(C–P) = 17.1, CHMe_2), 30.05 (s, CMe_3), 34.45 (s, *C*HMe$_2$), 38.93 (s, *C*Me$_3$), 178.65 (d, ^1J(C–P) = 33.7, P=CH), 195.72 (d, ^2J(C–P) = 9.6, cis CO), 198.91 (d, ^2J(C–P) = 27.7, trans CO); ^{1}H NMR (C_6D_6) δ 0.96 (dd, ^3J(H–H) = 6.6, ^4J(H–P) = 1.7, CHMe_2), 0.97 (d, ^3J(H–P) = 14.3, CMe_3), 3.0 (m, *C*HMe$_2$), 7.73 (dd, ^2J(H–P) = 18.6, ^3J(H–H) = 11.7, P=CH); IR (decalin) ν(CO) 2070 (m), 1950 (vs) cm^{-1}; mass spectrum (^{184}W) *m/z* 468 (M, 55), 328 (M – 5CO, 100). Anal. Calcd for $C_{13}H_{17}O_5PW$: C, 33.36; H, 3.66. Found: C, 33.79; H, 3.51.

(Phenylneopentylidenephosphine)pentacarbonyltungsten (15(*Z*),(*E*)). Trimethylacetaldehyde (1.1 mmol) was reacted with the anion of **1a** at room temperature for 45 min: yield 0.34 g (68%) of a mixture of the isomers **15(*Z*)** and **15(*E*)**; isomer ratio 9:1. **15(*Z*)** (mixture with **15(*E*)**): ^{31}P NMR (C_6D_6) δ 185.0 ($^1J(^{183}W-^{31}P)$ = 253.9); ^{1}H NMR (C_6D_6) δ 1.14 (d, ^4J(H–P) = 1.8, CMe_3), 8.35 (d, ^2J(H–P) = 23.2, P=CH); ^{13}C NMR (C_6D_6) δ 31.50 (d, ^3J(C–P) = 13.1, CMe_3), 38.23 (s, *C*Me$_3$), 192.75 (d, ^1J(C–P) = 34.22, P=CH), 196.00 (d, ^2J(C–P) = 9.6, cis CO), 198.92 (d, ^2J(C–P) = 28.1, trans CO); mass spectrum (^{184}W) *m/z* 502 (M, 43), 362 (M – 5CO, 83), 348 (100). **15(*E*)**: ^{31}P NMR (C_6D_6) δ 180.6.

(*tert*-Butylneopentylidenephosphine)pentacarbonyltungsten (16). Trimethylacetaldehyde (3 mmol) was reacted with the anion of **1b** between −70 °C and room temperature. **16**: yield 0.42 g (87%); yellow oil; ^{31}P NMR (pentane) δ 228.2 ($^1J(^{183}W-^{31}P)$ = 245.4); ^{1}H NMR (C_6D_6) δ 1.04 (d, ^3J(H–P) = 14.1, P-CMe_3), 1.16 (s, CMe_3), 8.51 (d, ^2J(H–P) = 24.4, P=CH); ^{13}C NMR (C_6D_6) δ 31.03 (d, ^2J(C–P) = 2.5, PCMe_3), 31.91 (d, ^3J(C–P) = 12.1, CCMe_3), 37.99 (s, *C*Me$_3$), 40.20 (d, ^1J(C–P) = 6.5, *C*Me$_3$), 187.49 (d, ^1J(C–P) = 27.2, P=CH), 196.77 (d, ^2J(C–P) = 9.0, cis CO), 198.61 (d, ^2J(C–P) = 27.8, trans CO); IR (decalin) ν(CO) 2070 (m), 1950 (vs) cm^{-1}; mass spectrum (^{184}W) *m/z* 482 (M, 57), 354 (100).

Synthesis of Phosphaalkene Complexes. Method B. Complex **2a** (1 mmol), the appropriate carbonyl compound, and DBO (1 mmol) were stirred in pentane–ether (2:1) for 0.5 h at room temperature. The reaction mixture was then directly chromatographed on a silica gel column with pentane as eluent. Note: the synthesis of each phosphaalkene complex can be generally performed as well via method A or method B.

(Phenylisopropylidenephosphine)pentacarbonylmolybdenum (7). Acetone (7 mmol) reacts with **2a** to give the corresponding phosphaalkene complex **7** in 56% yield (0.22 g). **7**: colorless oil; ^{31}P NMR (C_6D_6) δ 197.5; ^{1}H NMR (C_6D_6) δ 1.32 (d, ^3J(H–P) = 23.5, CH_3), 1.42 (d, ^3J(H–P) = 30.2, CH_3); ^{13}C NMR (C_6D_6) δ 26.15 (d, ^2J(C–P) = 23.1, CH_3), 26.50 (d, ^2J(C–P) = 12.1, CH_3), 187.46 (d, ^1J(C–P) = 33.7, P=*C*Me$_2$), 204.76 (d, ^2J(C–P) = 12.1, cis CO), 210.68 (d, ^2J(C–P) = 29.7, trans CO); IR (decalin) ν(CO) 2075 (m), 1955 (vs) cm^{-1}; mass spectrum (^{98}Mo) *m/z* 388 (M, 64), 248 (M – 5CO, 100).

(Phenylcyclopentylidenephosphine)pentacarbonylmolybdenum (8). Cyclopentanone (6 mmol) reacts with **2a** to give the corresponding phosphaalkene complex **8** in 37% yield (0.15 g). **8**: colorless oil; ^{31}P NMR (C_6D_6) δ 178.7; ^{1}H NMR (C_6D_6) δ 1.2–1.5 (m, 4 H, CH_2), 2.22 (m, ^3J(H–P) = 24.4, =CCH_2), 2.67 (m, ^3J(H–P) = 25.3, =CCH_2); ^{13}C NMR (C_6D_6) δ 27.11, 27.33 (2 CH_2), 37.95 (d, ^2J(C–P) = 17.1, =*C*CH$_2$), 39.97 (d, ^2J(C–P) = 11.6, =*C*CH$_2$), 198.9 (d, ^1J(C–P) = 35.7, P=*C*), 204.8 (d, ^2J(C–P) = 12.1, cis CO); IR (CCl_4) ν(CO) 2075 (m), 1955 (vs) cm^{-1}; mass spectrum (^{98}Mo) *m/z* 414 (M, 13), 272 (100).

Isomerization of the Phosphaalkene 11 to the Vinylphosphine (12). Complex **1a** (1 mmol), acetone (5 mmol), and DBO (2 mmol) were stirred in THF for 2 h at room temperature. The initial formation of **11**[1] was monitored by ^{31}P NMR spectroscopy. After evaporation of the solvent, the final product was purified by column chromatography with hexane as eluent. **12**: yield 0.24 g (51%); colorless solid; mp 60 °C (pentane); ^{31}P NMR (hexane) δ −6.4 ($^1J(^{183}W-^{31}P)$ = 231.9); ^{1}H NMR (C_6D_6) δ 1.44 (d, ^3J(H–P) = 11.1, CH_3), 5.12 (d, ^3J(H–P) = 39.8, =CH), 5.36 (d, ^3J(H–P) = 19.9, =CH), 5.73 (d, ^1J(H–P) = 344.1, PH); ^{13}C NMR (C_6D_6) 21.25 (d, ^2J(C–P) = 10.6, Me), 196.59 (d, ^2J(C–P) = 7.0, cis CO), 199.18 (d, ^2J(C–P) = 20.6, trans CO); IR (decalin) ν(CO) 2070 (m), 1945 (vs) cm^{-1}; mass spectrum (^{184}W) *m/z* 474 (M, 36), 332 (100). Anal. Calcd for $C_{14}H_{11}O_5PW$: C, 35.47; H, 2.34. Found: C, 35.64; H, 2.20.

Phosphaalkene Complex Trapping Reactions. A solution of **1** (**2**) (1 mmol) in THF was cooled to −78 °C. *n*-BuLi (0.7 mL, 1.6 M solution in hexane) was then added. After a few minutes, an excess (1:10) of the trapping reagent (MeOH or 2,3-dimethyl-1,3-butadiene) and the carbonyl compound (1 mmol) were added. The reaction mixture was then warmed to room temperature and hydrolyzed with water. After extraction with ether and evaporation of the solvent, the final product was purified by chromatography on a silica gel column.

[Methyl (2-oxo-1-methylpropyl)phenylphosphinite]pentacarbonyltungsten (10). Complex **10** was purified by chromatography with hexane–ether (95:5) as eluent: yield 0.42 g (80%) of a mixture of two isomers (ratio 6:4); colorless solid. **10**, major isomer: ^{31}P NMR (C_6D_6) δ 128.3 ($^1J(^{183}W-^{31}P)$ = 280.8); ^{1}H NMR (C_6D_6) δ 0.92 (dd, ^3J(H–P) = 15.4, ^3J(H–H) = 7.2, CHCH_3), 1.68 (s, COMe), 3.08 (dq, ^2J(H–P) = 3.8, PCH), 3.27 (d, ^3J(H–P) = 13.14, OCH_3); ^{13}C NMR (C_6D_6) δ 12.05 (s, CHCH_3),

30.81 (s, $COCH_3$), 55.51 (s), 56.21 (d, J(C–P) = 20.1), 196.81 (d, ^2J(C–P) = 7.5, cis CO), 198.54 (d, ^2J(C–P) = 26.7, trans CO), 205.17 (s, COMe); IR (decalin) ν(CO) 2070 (m), 1950 (sh) 1940 (vs) cm^{-1}, ν(COMe) 1715 cm^{-1}; mass spectrum (^{184}W) m/z 506 (M – CO, 62), 394 (M – 5CO, 100). **10**, minor isomer: ^{31}P NMR (C_6D_6) δ 133.1; ^1H NMR (C_6D_6) δ 1.01 (dd, ^3J(H–P) = 18.5, ^3J(H–H) = 7.2, $CHCH_3$), 1.57 (s, $COCH_3$), 2.95 (m, PCH), 3.14 (d, ^3J(H–P) = 13.0, OCH_3).

[Methyl isobutylphenylphosphinite]pentacarbonylmolybdenum (22). Complex **22** was chromatographed with hexane. **22**: yield 0.35 g (81%); colorless solid; mp <50 °C; ^{31}P NMR (CH_2Cl_2) δ 151.2; ^1H NMR (C_6D_6) δ 0.80 (d, ^3J(H–H) = 6.6, $CH(CH_3)_2$), 1.7–1.9 (m, 2 H, PCH_2), 2.11 (m, 1 H, CH), 3.02 (d, ^3J(H–P) = 12.7, OCH_3); IR (decalin) ν(CO) 2075 (m), 1950 (vs) cm^{-1}; mass spectrum (^{98}Mo) m/z 434 (M, 11), 294 (M – 5CO, 100).

[Methyl isobutyl-*tert*-butylphosphinite]pentacarbonylmolybdenum (23). Complex **23** is purified by chromatography with hexane as eluent. **23**: yield 0.34 g (83%); colorless oil; ^{31}P NMR (CH_2Cl_2) δ 179.5; ^1H NMR (C_6D_6) δ 0.88 (d, ^3J(H–P) = 14.1, $C(CH_3)_3$), 0.97 (d, ^3J(H–H) = 5.5, $CH(CH_3)_2$), 1.4 (m, 1 H), 1.7 (m, 1 H), 2.25 (m, 1 H), 3.21 (d, ^3J(H–P) = 12.3, OCH_3); IR (decalin) ν(CO) 2070 (m), 1945 (vs) cm^{-1}; mass spectrum (^{98}Mo) m/z 414 (M, 20), 330 (M – 3CO, 74), 300 (100).

[1-Phenyl-2-(2-thienyl)-4,5-dimethyl-1,2,3,6-tetrahydrophosphorine]pentacarbonyltungsten (20). The reaction takes place between –78 °C and room temperature. Chromatography with hexane as eluent gives **20**: yield 0.24 g (39%); colorless solid; mp 89 °C (hexane); ^{31}P NMR (hexane) δ –1.2 ($^1J(^{183}W–^{31}P)$ = 249.0); ^1H NMR (C_6D_6) δ 1.25 (s, CH_3), 1.54 (s, CH_3), 2.0 (m, CH_2), 2.70 (m, CH_2), 3.42 (dt, ^2J(H–P) = 8.8, PCH); ^{13}C NMR (C_6D_6) δ 20.28 (s, CH_3), 21.28 (d, ^3J(C–P) = 7.5, CH_3), 32.29 (d, ^1J(C–P) = 24.2, PCH_2), 36.79 (s), 38.40 (d, J(C–P) = 22.1), 196.86 (d, ^2J(C–P) = 6.5, cis CO), 199.29 (d, ^2J(C–P) = 22.6, trans CO); IR (decalin) ν(CO) 2070 (m), 1950 (s), 1940 (s), 1930 (s) cm^{-1}; mass spectrum (^{184}W) m/z 610 (M, 13), 470 (M – 5CO, 100). Anal. Calcd for $C_{22}H_{19}O_5PSW$: C, 43.30; H, 3.14. Found: C, 43.54; H, 3.04.

[1-Phenyl-2-(*p*-chlorophenyl)-4,5-dimethyl-1,2,3,6-tetrahydrophosphorine]pentacarbonylmolybdenum (21). Complex **21** was purified by column chromatography with hexane as eluent. **21**: yield 0.34 g (61%); colorless solid; mp 115 °C; ^{31}P NMR (CH_2Cl_2) δ 13.5; ^1H NMR (C_6D_6) δ 1.34 (s, CH_3), 1.61 (s, CH_3), 2.1 (m, 2 H), 2.38 (*AB*, $^2J(H_A–H_B)$ = 17.6, 1 H, PCH_2), 2.65 (*AB*, ^2J(H–P) = 8.0, 1 H, PCH_2), 2.8 (m, 1 H, PCH); ^{13}C NMR (C_6D_6) δ 19.67 (s, CH_3), 21.33 (d, ^3J(C–P) = 7.0, CH_3), 31.84 (d, J(C–P) = 20.1), 36.36 (s), 42.69 (d, J(C–P) = 15.6), 205.61 (d, ^2J(C–P) = 9.1, cis CO), 209.67 (d, ^2J(C–P) = 24.2, trans CO); IR (CCl_4) ν(CO) 2070 (m), 1950 (vs) cm^{-1}; mass spectrum (^{98}Mo, ^{35}Cl) m/z 552 (M, 9), 412 (M – 5CO, 72), 314 (100).

Decomplexation of the "$Mo(CO)_5$" Complexes with Sulfur. The molybdenum complex (**21–23**) was heated with an excess of S_8 (10:1 ratio) in toluene at 100 °C for 12 h. After evaporation of the solvent, the final product (**24–26**) was purified by chromatography with hexane as eluent. **24**: yield 85%; colorless solid; mp 118 °C; ^{31}P NMR ($CDCl_3$) δ 35.6; ^1H NMR (C_6D_6) δ 1.51 (d, J = 5.1, CH_3), 1.59 (s, CH_3), 2.0–2.4 (m, 2 H), 2.76 (m, 1 H), 3.05 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.52 (s, CH_3), 21.76 (d, ^3J(C–P) = 11.6, CH_3), 36.63 (s, CH_2), 38.51 (d, ^1J(C–P) = 51.8, PCH_2), 43.09 (d, ^1J(C–P) = 46.3, PCH); mass spectrum (^{35}Cl) m/z 346 (M, 79), 205 (100). **25**: yield 80%; colorless oil; ^{31}P NMR (toluene) δ 93.2; ^1H NMR (C_6D_6) δ 0.7 (d, ^3J(H–H) = 6.7, $CHCH_3$), 0.94 (d, ^3J(H–H) = 6.6, $CHCH_3$), 1.7–2.1 (m, 2 H), 2.3 (m, 1 H), 3.23 (d, ^3J(H–P) = 13.7, OCH_3); mass spectrum m/z 228 (M, 36), 172 (89), 139 (100). **26**: yield 78%; colorless oil; ^{31}P NMR ($CDCl_3$) δ 114.7; ^1H NMR ($CDCl_3$) δ 1.00 (d, ^3J(H–H) = 6.6, $CHCH_3$), 1.07 (d, ^3J(H–H) = 6.7, $CHCH_3$), 1.19 (d, ^3J(H–P) = 16.4, $C(CH_3)_3$), 1.75 (m, 2 H), 2.3 (m, 1 H), 3.68 (d, ^3J(H–P) = 12.7, OCH_3); mass spectrum m/z 208 (M, 87), 152 (100). Anal. Calcd for $C_9H_{21}OPS$: C, 51.90; H, 10.16. Found: C, 51.72; H, 9.92.

X-ray Structure Determination for 13(*Z*). Crystals of **13**(*Z*), $C_{15}H_{13}O_5PW$, were grown at –18 °C from a pentane solution of the compound. Data were collected at 18 ± 1° on an Enraf-Nonius CAD4 diffractometer. The crystal structure was solved and refined with use of the Enraf-Nonius-supplied SDP package. The compound crystallizes in space group $C2/c$, with a = 26.495 (3) Å, b = 6.597 (1) Å, c = 20.280 (2) Å, β = 94.37 (1)°, V = 3534.5 (1.3) Å^3, Z = 8, d(calc) = 1.843 g/cm^3, Mo Kα radiation (λ = 0.71073 Å), graphite monochromator, μ = 68.1 cm^{-1}, and F(000) = 1856. A total of 5099 unique reflections were recorded in the range 2° ≤ 2θ ≤ 60°, of which 3111 were considered as unobserved ($F^2 < 3\sigma(F^2)$), leaving 2988 for solution and refinement. The structure was solved by Patterson methods, yielding a solution for the tungsten and phosphorus atoms. The hydrogen atoms were included as fixed contributions 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 factor equal to 0.08. The final R factors were R = 0.047, R_w = 0.071, and GOF = 1.43.

X-ray Structure Determination for 14. Crystals of **14**, $C_{13}H_{17}O_5PW$, were grown at –18 °C from a pentane solution of the compound. Data were collected at 18 ± 1° on an Enraf-Nonius CAD4 diffractometer. The crystal structure was solved and refined with use of the Enraf-Nonius-supplied SDP package. The compound crystallizes in space group $P2_1/n$, with a = 6.686 (1) Å, b = 16.201 (2) Å, c = 16.311 (2) Å, β = 93.98 (1)°, V = 1762.49 (71) Å^3, Z = 4, d(calc) = 1.764 g/cm^3, Mo Kα radiation (λ = 0.71073 Å), graphite monochromator, μ = 68.0 cm^{-1}, and F(000) = 896. A total of 5140 unique reflections were recorded in the range 2° ≤ 2θ ≤ 60°, of which 2135 were considered as unobserved ($F \leq 3\sigma(F)$), leaving 3005 for solution and refinement. The structure was solved by Patterson methods, yielding a solution for the tungsten and phosphorus atoms. The hydrogen atoms were included as fixed contributions 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 factor equal to 0.08. The final R factors were R = 0.031, R_w = 0.055, and GOF = 1.06.

Registry No. **1a**, 116972-70-4; **1a** (lithium salt), 124992-19-4; **1b**, 124992-14-9; **1b** (lithium salt), 124992-20-7; **1c**, 116972-79-3; **1c** (lithium salt), 124992-21-8; **2a**, 124992-15-0; **2a** (lithium salt), 124992-22-9; **2b**, 124992-16-1; **2b** (lithium salt), 124992-23-0; **3**(*E*), 124992-24-1; **3**(*Z*), 125074-76-2; **4**, 124992-25-2; **5**, 125023-06-5; **6**, 124992-26-3; **7**, 124992-30-9; **8**, 124992-31-0; **10** (isomer 1), 124992-33-2; **10** (isomer 2), 125074-78-4; **11**, 116972-71-5; **12**, 124992-32-1; **13**(*Z*), 117064-22-9; **13**(*E*), 116972-73-7; **14**(*Z*), 124992-27-4; **15**(*Z*), 124992-28-5; **15**(*E*), 125074-77-3; **16**(*Z*), 124992-29-6; **20**, 124992-34-3; **21**, 124992-35-4; **22**, 124992-36-5; **23**, 124992-37-6; **24**, 124992-12-7; **25**, 118051-13-1; **26**, 124992-13-8; $W(CO)_6$, 14040-11-0; $Mo(CO)_6$, 13939-06-5; $(PhPCl_2)W(CO)_5$, 18461-46-6; $(t\text{-}BuPCl_2)W(CO)_5$, 124992-17-2; $(PhPCl_2)Mo(CO)_5$, 21485-20-1; $(t\text{-}BuPCl_2)Mo(CO)_5$, 124992-18-3; $(PhPH_2)W(CO)_5$, 61300-75-2; $(t\text{-}BuPH_2)W(CO)_5$, 103782-58-7; $(PhPH_2)Mo(CO)_5$, 72868-86-1; $(t\text{-}BuPH_2)Mo(CO)_5$, 103782-57-6; $PhPCl_2$, 644-97-3; t-$BuPCl_2$, 25979-07-1; Me_2CHCHO, 78-84-2; Me_3CCHO, 630-19-3; MeC(O)C(O)Me, 431-03-8; $CH_2=C(CH_3)C(CH_3)=CH_2$, 513-81-5; $(EtO)_2P(O)Cl$, 814-49-3; 2-adamantanone, 700-58-3; acetone, 67-64-1; cyclopentanone, 120-92-3; 2-thiophenecarboxaldehyde, 98-03-3; 4-chlorobenzaldehyde, 104-88-1; 2-butanone, 78-93-3.

Supplementary Material Available: Tables of bond distances and angles, positional parameters, and thermal parameters for **13**(*Z*) and **14** (8 pages); tables of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.