Phospha-Wittig reaction in the synthesis of 1-phosphadienes and (.eta.4-1-phosphadiene)tricarbonyliron complexes from .alpha.,.beta.-unsaturated aldehydes

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"Phospha-Wittig" Reaction in the Synthesis of 1-Phosphadienes and (η^4-1-Phosphadiene)tricarbonyliron Complexes from α,β-Unsaturated Aldehydes

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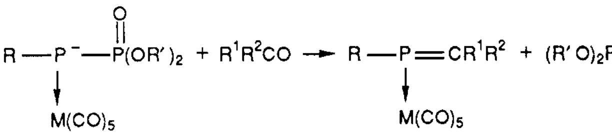
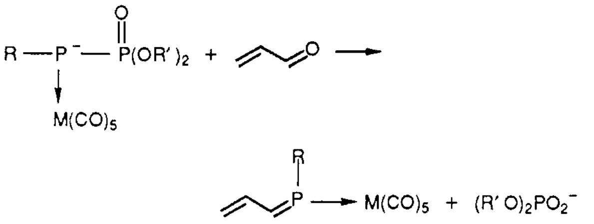
The reaction of the "phospha-Wittig" reagents $[(RO)_2P(O)\text{-}P^-R]W(CO)_5$ with α,β-unsaturated aldehydes yields the corresponding 1-phosphadiene $P\text{-}W(CO)_5$ complexes. These unstable species either undergo a conrotatory ring closure to give stable 1,2-dihydrophosphete $P\text{-}W(CO)_5$ complexes or are trapped by conjugated dienes to give the [2 + 4] cycloadducts via their P=C double bond, which acts as a dienophile. The reaction of the same "phospha-Wittig" reagents with the η^2-(C=C)$Fe(CO)_4$ complexes of α,β-unsaturated aldehydes first gives the η^1-P-$W(CO)_5$, η^2-(P=C)$Fe(CO)_4$ complexes of 1-phosphadienes, which then lose CO upon heating to yield the corresponding η^4-$Fe(CO)_3$ complexes. The structure of one such η^4 complex has been investigated by X-ray analysis. It shows a strictly planar phosphadiene unit. The Fe–PC_3 plane distance is 1.6672 (7) Å, close to the normal values for (η^4-diene)iron complexes. The tungsten atom is on the other side of this plane at 1.8528 (2) Å, and the substituent at phosphorus is almost coplanar with the PC_3 unit.

Recently, we discovered what we called the "phospha-Wittig" reaction[1] in which a carbonyl compound is directly converted into a phosphaalkene complex (eq 1). As a logical extension of this work, we decided to investigate the reaction of the phospha-Wittig reagents with α,β-unsaturated carbonyl compounds. The expected products were the very reactive 1-phosphadiene complexes (eq 2), the reactions and stabilization of which are described hereafter.



$$\underset{\downarrow\;M(CO)_5}{R-P^-}-\overset{O}{\overset{\|}{P}}(OR')_2 + R^1R^2CO \longrightarrow \underset{\downarrow\;M(CO)_5}{R-P{=}CR^1R^2} + (R'O)_2PO_2^- \qquad (1)$$

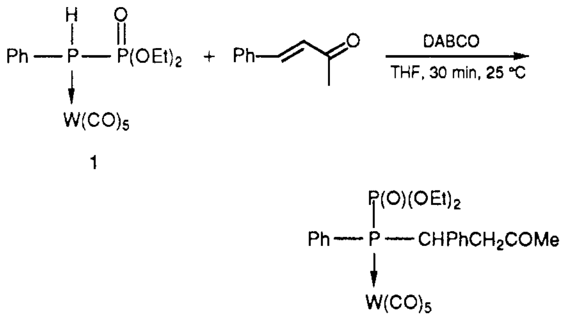
M = Mo, W



(2)

Results and Discussion

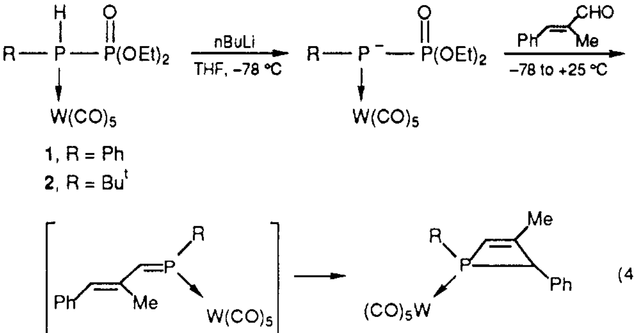
For practical reasons, we restricted our investigations to two readily available phospha-Wittig reagents in the tungsten series with *P*-phenyl and *P*-*tert*-butyl substituents **1** and **2**.[1,2] We soon discovered that the reactions of **1** take place at the C=C double bond of α,β-unsaturated ketones (eq 3). Complexes **3a,b** were separated and fully characterized. Apart from frontier orbital considerations, we feel that steric hindrance at the carbonyl carbon plays a great role in this 1,4 conjugate addition. We have already noticed that the phospha-Wittig reaction is very sensitive to steric factors.[1] With disubstituted α,β-unsaturated aldehydes, on the contrary, the phospha-Wittig reagents give the expected 1,2-addition on the carbonyl group, which ultimately yields the desired 1-phosphadienes. If no trapping reagent is added in the reaction medium, the phosphadienes either decompose or cyclize to give 1,2-dihydrophosphetes (eq 4). That the R substituents at phosphorus are trans to the C–C central bond of the dienes in the intermediate 1-phosphadienes is unambiguously demonstrated by the X-ray crystal structure analysis of a (η^4-1-phosphadiene)tricarbonyliron complex that is reported hereafter. We had already noticed in our preceding work[1] that the steric bulk of the $W(CO)_5$ complexing group apparently plays no role in the determination of the preferred geometry of the phosphaalkene bond. The spontaneous cyclization of these 1-phosphadienes has been



1

(3)

3a,b



1, R = Ph
2, R = Bu^t

4, R = Ph (65%)
5, R = Bu^t (69%)

(4)

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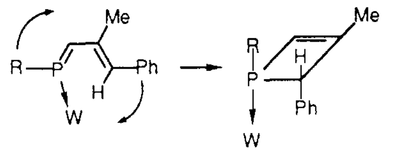
[1] Marinetti, A.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1382. Marinetti, A.; Bauer, S.; Ricard, L.; Mathey, F. *Organometallics*, in press.

[2] Marinetti, A.; Mathey, F. *Tetrahedron* **1989**, *45*, 3061.

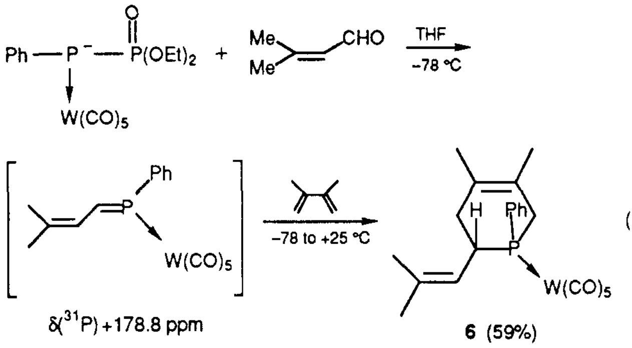
previously mentioned by Neilson[3] and us.[4] However, no discussion of the stereochemistry of the ring closure was possible. Here, the cyclization gives only one isomeric 1,2-dihydrophosphete in both cases. The two rings are characterized by similar ($^2J(H\text{-}Csp^3\text{-}P)$) coupling constants, 9.4 and 8.4 Hz for **4** and **5**, respectively. According to our previous work[4] and to a X-ray crystal structure analysis of **4**,[5] this means that, in both compounds, H is trans to W. As a consequence, the ring closure is conrotatory (eq 5) and follows the Woodward–Hoffmann rules.



(5)

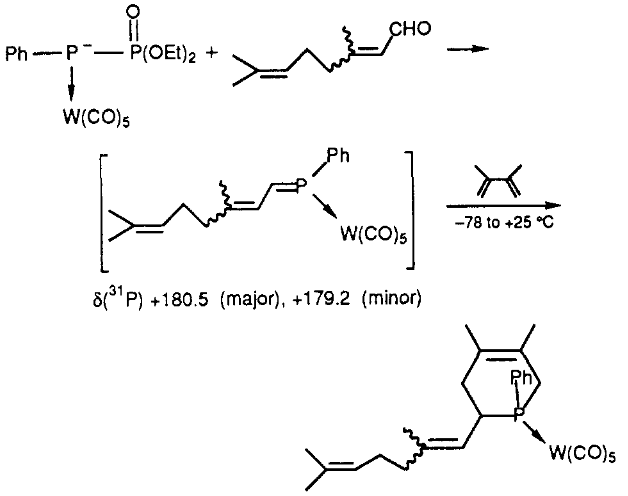
It is interesting to note here that a similar conrotatory opening takes place in the $P_2W_2(CO)_{10}$ complexes of 1,2-dihydro-1,2-diphosphetes.[6]

With other aldehydes such as dimethylacrolein and citral, it is possible to monitor at low temperature by ^{31}P NMR spectroscopy the formation of the expected 1-phosphadienes. If a trapping reagent such as 2,3-dimethylbutadiene is added to the reaction medium, then the 1-phosphadienes give the corresponding [2 + 4] cycloadducts as ordinary phosphaalkenes (eqs 6 and 7).



(6)

6 (59%)

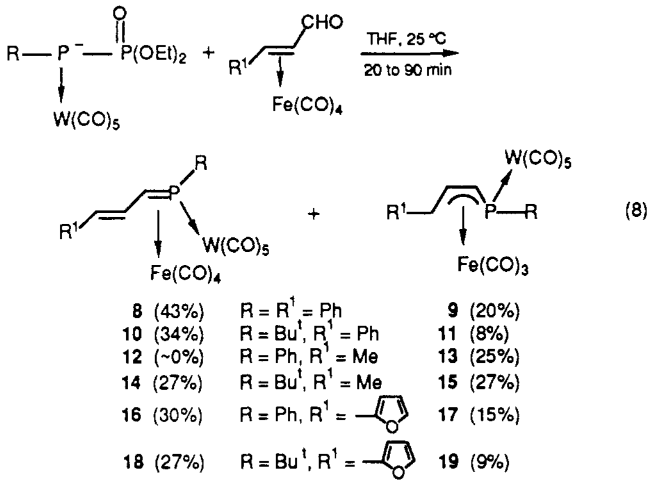


(7)

7a,b (89%)

When starting with dimethylacrolein, only one isomeric [2 + 4] cycloadduct, **6**, was obtained, thus confirming that, in each case, only one isomeric 1-phosphadiene is formed via the phospha-Wittig reaction.

To collect more data on the structural features of these elusive 1-phosphadienes, we decided to attempt their stabilization by η^4 complexation with iron tricarbonyl. Indeed, we has already observed a stable (η^4-1-phosphadiene)tetracarbonyltungsten complex[7] that spontaneously cyclized upon decomplexation. We chose to study the reaction of the phospha-Wittig reagents with the η^2-(C=C)$Fe(CO)_4$ complexes of α,β-unsaturated aldehydes. In every cases, we obtained two types of 1-phosphadiene complexes (eq 8). In most cases, the η^2-$Fe(CO)_4$ complexes were directly converted into the η^4-$Fe(CO)_3$ complexes by simple heating at ca. 80–90 °C for 1–2 h. However, **8** and **10** were completely characterized. We will use **8** as an example. The ^{31}P chemical shift at high field (−37 ppm) clearly demonstrates that the P=C double bond is π-complexed. The IR spectrum (Decalin) shows the superimposition of the CO stretching frequencies corresponding to the $W(CO)_5$ [ν(CO) 2070 m and 1945 vs] and $Fe(CO)_4$ [ν(CO) 2100 m, 2042 m, 2034 s, and 2010 m] complexing groups (for comparison, see ref 8). The ^1H NMR spectrum shows one "vinylic" proton (δ 4.43 in C_6D_6), and the ^{13}C NMR spectrum one "vinylic" carbon (δ 51.5 in C_6D_6) shifted to high fields. The mass spectra of **8** and **9** are exactly similar, showing only the molecular peak of **9** (m/z 688). It is well-known that $Fe(CO)_4$ easily migrates along a conjugated system. Here, the migration takes place from a C=C to a P=C double bond, suggesting a higher complexing ability for the phosphaalkene bond. Similar η^1-P, η^2-P=C complexes have already been described in the literature.[9]



(8)

The η^4-complexation induces very characteristic changes in the NMR spectra of the complexes. The comparison between **8** and **9** is illustrative. The ^{31}P chemical shift of **9** is again at high fields as expected (−30.6 ppm in C_6D_6). More significantly, three "vinylic" protons and three "vinylic" carbons are now visible at high fields: $\delta(^1H)$ 3.39 (PhCH), 5.74 (PhCHCH), and 4.96 (PCH); $\delta(^{13}C)$ 68.30, 75.98, and 89.98 (C_6D_6). The IR spectrum is simpler: ν(CO) 2070 w and 1945 vs [$W(CO)_5$]; 2052 s, 2008 s, and 1982 w [$Fe(CO)_3$] (for comparison, see refs 8 and 10). A closer inspection of the ^1H NMR data gives a clue con-

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[5] The results of this X-ray crystal structure analysis are not reported here because they are very similar to those described in ref 4.

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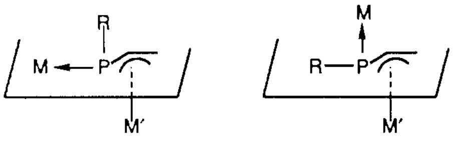
Table I. Positional Parameters and Their Estimated Standard Deviations for 15[a]

atom	*x*	*y*	*z*	*B*, Å^2
W	0.26960 (2)	0.01867 (2)	0.61114 (1)	2.830 (3)
Fe	0.10766 (6)	0.08895 (6)	0.85966 (4)	2.95 (1)
P	0.2546 (1)	−0.0047 (1)	0.77243 (8)	2.67 (2)
O9	0.2573 (5)	0.0967 (5)	1.0180 (3)	7.1 (1)
O10	0.1924 (5)	0.2870 (4)	0.7859 (3)	6.2 (1)
O11	−0.1094 (4)	0.1618 (5)	0.9627 (3)	6.3 (1)
O12	0.4068 (5)	−0.2008 (4)	0.5772 (3)	6.9 (1)
O13	0.0038 (5)	−0.1065 (5)	0.5772 (4)	6.5 (1)
O14	0.1072 (5)	0.2309 (4)	0.6015 (3)	6.2 (1)
O15	0.5396 (4)	0.1387 (4)	0.6337 (3)	6.0 (1)
O16	0.3019 (6)	0.0549 (6)	0.4175 (3)	6.8 (1)
C1	0.1221 (5)	−0.0700 (4)	0.8231 (4)	3.6 (1)
C2	−0.0054 (6)	−0.0307 (5)	0.8072 (4)	4.0 (1)
C3	−0.0272 (5)	0.0578 (5)	0.7574 (4)	3.7 (1)
C4	−0.1610 (6)	0.1089 (7)	0.7506 (5)	6.0 (2)
C5	0.4086 (5)	−0.0471 (5)	0.8308 (3)	3.7 (1)
C6	0.4846 (6)	0.0552 (7)	0.8521 (4)	4.7 (1)
C7	0.3827 (6)	−0.1124 (6)	0.9089 (4)	4.8 (1)
C8	0.4932 (6)	−0.1130 (6)	0.7724 (4)	5.0 (1)
C9	0.2046 (6)	0.0897 (6)	0.9545 (4)	4.7 (1)
C10	0.1574 (5)	0.2123 (5)	0.8144 (4)	3.8 (1)
C11	−0.0250 (5)	0.1317 (5)	0.9231 (4)	4.1 (1)
C12	0.3608 (6)	−0.1227 (5)	0.5934 (4)	4.1 (1)
C13	0.0992 (6)	−0.0614 (5)	0.5907 (4)	3.9 (1)
C14	0.1686 (6)	0.1564 (5)	0.6095 (3)	3.9 (1)
C15	0.4415 (6)	0.0963 (5)	0.6280 (4)	3.9 (1)
C16	0.2885 (6)	0.0411 (6)	0.4886 (4)	4.4 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

cerning the stereochemistry at phosphorus. We have already studied in depth such a problem with η^3-phosphaallyl complexes. Two stereochemistries are possible, and both have been found in this case. Stereochemistry A has been established by X-ray crystal structure analysis for M=W(CO)$_5$ and M′=CpFe(CO).[11] It is characterized by a huge ^2J(*H*-C-*P*) coupling, ca. 30 Hz. Stereochemistry B has also been established by X-ray crystal structure analysis for M=W(CO)$_5$ and M′=CpMo(CO)$_2$.[12] In that case, the ^2J(*H*-C-*P*) coupling is close to 0 Hz. For all the η^4-Fe(CO)$_3$ complexes such as **9**, the PC*H* proton shows no coupling with phosphorus. We thus predict a stereochemistry similar to B for the (η^4-1-phosphadiene)Fe(CO)$_3$ complexes. This is indeed the case as shown by the X-ray crystal structure analysis of complex **15**. Before discussing more in depth the structural features of **15**, it is appropriate to mention that the only previously described η^4-1-phosphadiene complex with M=W(CO)$_5$ and M′=W(CO)$_4$ has the other stereochemistry (A).[7] The most significant structural data of **15** are given in the caption of Figure 1. A listing of positional parameters is given in Table I. The PC$_1$C$_2$C$_3$ moiety is planar as expected. The tungsten atom lies 1.8528 (2) Å above and the iron atom −1.6672 (7) Å below this plane. The distance of iron to this plane is very similar to those found in (η^4-diene)Fe(CO)$_3$ complexes (ca. 1.64 Å).[13] As in the diene complexes, the substituents at the terminal syn positions are displaced toward iron: the distances to the plane are respectively −0.1801 (81) and −0.5608 (58) Å for C$_4$ and C$_5$. The P-C$_1$ bond is intermediate between a single and a double bond, as is usual for such complexes.[7,9,11,12] All in all, it can be stated that **15** is remarkably similar to classical (η^4-diene)Fe(CO)$_3$ complexes except in the vicinity of phosphorus. At this point of our research program, it can be concluded that the reaction of phospha-Wittig reagents with α,β-unsaturated aldehydes provides a versatile access to a variety of reactive 1-phosphadienes. Previously, only a deactivated 1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphadiene and a more reactive silyl-substituted 1-phosphadiene had been respectively described by Appel[14] and Neilson.[15] Using this new route, we have been able to demonstrate the conrotatory ring closure of such species, to trap them as [2 + 4] cycloadducts with conjugated dienes, and to stabilize



A (R up, M in plane) B (R in plane, M up)

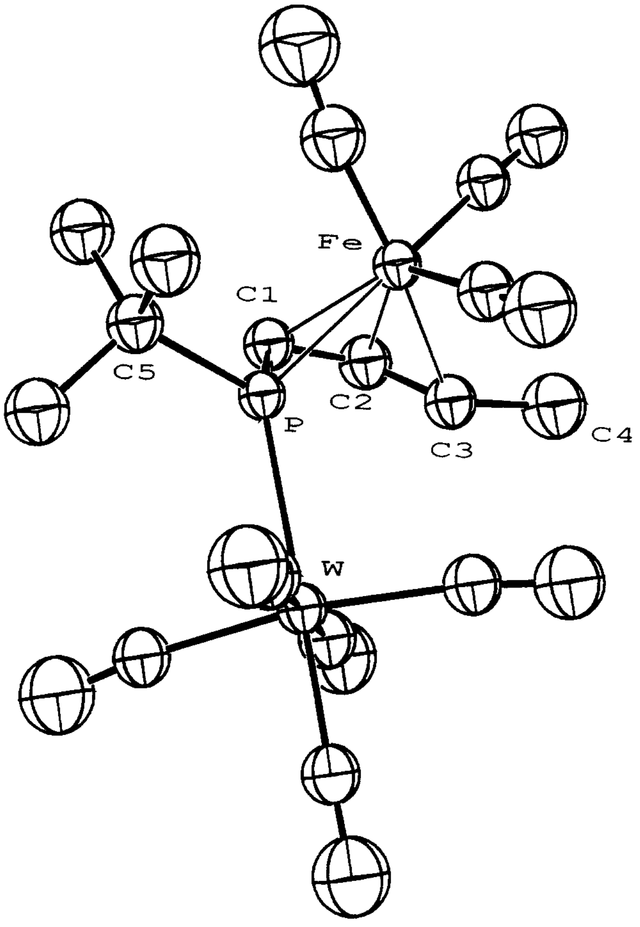


Figure 1. ORTEP representation of C$_{16}$H$_{15}$O$_8$PFeW (**15**) with thermal ellipsoids at the 50% probability level; hydrogen atoms are omitted. Principal bond distances: W-P, 2.591 (1); Fe-P, 2.378 (1); Fe-C$_1$, 2.107 (5); Fe-C$_2$, 2.078 (5); Fe-C$_3$, 2.155 (5); P-C$_1$, 1.789 (5); P-C$_5$, 1.895 (5); C$_1$-C$_2$, 1.416 (8); C$_2$-C$_3$, 1.391 (9) Å. Selected bond angles: W-P-Fe, 124.57 (5); W-P-C$_1$, 123.7 (2); W-P-C$_5$, 117.3 (2); Fe-P-C$_1$, 58.7 (2); Fe-P-C$_5$, 112.5 (2); C$_1$-P-C$_5$, 106.0 (3); P-C$_1$-C$_2$, 117.2 (4); C$_1$-C$_2$-C$_3$, 121.8 (5); C$_2$-C$_3$-C$_4$, 121.6 (5); P-Fe-C$_1$, 46.5 (1); C$_1$-Fe-C$_2$, 39.5 (2); C$_2$-Fe-C$_3$, 38.3 (2)°.

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them as original η^2-Fe(CO)$_4$ and η^4-Fe(CO)$_3$ complexes.

Experimental Section

All reactions were carried out under argon. Chromatographic separations were performed on silica gel column (70–230 mesh, Merck). All commercially available reagents were used as received from the suppliers. NMR spectra were recorded on a Brucker AC 200 SY spectrometer operating at 200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C and on a Brucker 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). 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. Compounds **7**, **17**, and **19** are poorly stable and were not analyzed.

1,4-Addition of Complex 1 to 4-Phenyl-3-buten-2-one. 1,4-Diazabicyclo[2.2.2]octane (DABCO, 0.11 g, 1.0 mmol) was added at room temperature to a solution of complex **1** (0.57 g, 1.0 mmol) and 4-phenyl-3-buten-2-one (0.15 g, 1.0 mmol) in THF. After 30 min, the reaction mixture was hydrolyzed with water. After evaporation of the THF and extraction with ether, the final products were purified by chromatography with hexane/ether (60:40), yield 0.54 g (75%) of the mixture of two isomers **3a**,**b** (1:1 ratio). **3a** and **3b** were partially separated by chromatography, and each one was characterized separately.

3a: colorless solid; mp 114 °C; ^{31}P NMR (hexane/ether) δ 22.2 (*A*B, ^1J(P$_A$–P$_B$) = 70 Hz), 8.3 (A*B*, ^1J(^{183}W–^{31}P) = 242 Hz); ^{1}H NMR (C_6D_6) δ 0.76 (t, ^3J(H–H) = 7.0 Hz, CH$_2$C*H*$_3$), 1.10 (t, ^3J(H–H) = 7.0 Hz, CH$_2$C*H*$_3$), 1.42 (s, COCH$_3$), 2.81 (m, ^3J(H–H) = 10.4 Hz, *J* = 17.5 Hz, *J* = 3.8 Hz, 1 H, PC*H*Ph), 3.5–4.0 (m, 5 H, OC*H*$_2$CH$_3$ + C*H*$_2$CO (1 H)), 4.74 (m, 1 H, CH$_2$CO), 6.9–7.3, 8.2–8.4 (m, Ph); ^{13}C NMR (C_6D_6) δ 16.05 (d, ^3J(C–P) 8.05 Hz, CH$_2$CH$_3$), 16.20 (d, ^3J(C–P) = 6.5 Hz, CH$_2$CH$_3$), 29.89 (s, *C*H$_3$CO), 41.86 (d, ^1J(C–P) = 10.1 Hz, *C*HP), 46.57 (s, *C*H$_2$CO), 63.42 (d, ^2J(C–P) = 8.1 Hz, O*C*H$_2$), 63.84 (d, ^2J(C–P) = 7.5 Hz, O*C*H$_2$), 196.95 (d, ^2J(C–P) = 6.5 Hz, cis CO), 198.28 (d, ^2J(C–P) = 25.7 Hz, trans CO), 203.13 (d, ^3J(C–P) = 9.6 Hz, *C*OCH$_3$); IR (Decalin) ν(CO) 2070 (m), 1950 (vs), 1940 (vs), ν(COCH$_3$) 1730 cm^{-1}; mass spectrum (^{184}W), *m*/*e* (rel intensity) 687 (M – CO – 1, 14), 660 (M – 2CO, 21), 632 (M – 3CO, 7), 604 (M – 4CO, 9), 576 (M – 5CO, 15), 540 (23), 484 (100). Anal. Calcd for $C_{25}H_{26}O_9P_2W$: C, 41.92; H, 3.66. Found: C, 41.99; H, 3.54.

3b: colorless solid; mp 144 °C (ether); ^{31}P NMR (ether/CH$_2$Cl$_2$) δ 23.9 (*A*B, ^1J(P$_A$–P$_B$) = 51 Hz), 10.0 (A*B*); ^{1}H NMR (C_6D_6) δ 0.85 (t, ^3J(H–H) = 7.0 Hz, CH$_2$C*H*$_3$), 0.99 (t, ^3J(H–H) = 7.0 Hz, CH$_2$C*H*$_3$), 1.60 (s, C*H*$_3$CO), 3.4 (m, 2 H, PC*H*Ph + CH$_2$CO (1 H)), 3.6–4.0 (m, 4 H, OC*H*$_2$CH$_3$), 5.0 (m, 1 H, C*H*$_2$CO), 6.7–7.2, 8.0–8.1 (m, Ph); ^{13}C NMR (C_6D_6) δ 16.14 (s, CH$_2$CH$_3$), 16.24 (s, CH$_2$CH$_3$), 29.76 (s, *C*H$_3$CO), 41.71 (d, ^1J(C–P) = 17.6 Hz, P*C*HPh), 46.56 (d, ^2J(C–P) = 9.1 Hz, *C*H$_2$CO), 62.78 (d, ^2J(C–P) = 9.1 Hz, O*C*H$_2$), 64.64 (d, ^2J(C–P) = 7.5 Hz, O*C*H$_2$), 196.97 (d, ^2J(C–P) = 6.5 Hz, cis CO), 202.89 (d, ^3J(C–P) = 13.1 Hz, *C*OCH$_3$); IR (Decalin) ν(CO) 2070 (M), 1950 (vs), 1940 (vs), 1935 (vs), ν(COCH$_3$) 1730 cm^{-1}; mass spectrum (^{184}W), *m*/*e* (rel intensity) 687 (M – CO– 1, 11), 660 (M – 2CO, 28), 604 (M – 4CO, 13), 576 (M – 5CO, 14), 540 (28), 484 (100). Anal. Calcd for $C_{25}H_{26}O_9P_2W$: C, 41.92; H, 3.66. Found: C, 41.75; H, 3.46.

Reactions of Complexes 1 and 2 with α-Methylcinnamaldehyde (Reaction 4). A solution of complex **1** (or **2**) (1 mmol) in THF was cooled to –78 °C. nBuLi (0.7 mL, 1.6 M solution in hexane) was then added. After a few minutes, α-methylcinnamaldehyde (0.29 mL, 3 mmol) was added. The reaction mixture was then allowed to warm to room temperature. After hydrolysis, evaporation of the solvent, and extraction with ether, the final product was purified by chromatography with hexane/ether (99:1) as eluent.

4: yield 0.37 g (65%); colorless solid, mp 96 °C (pentane); ^{31}P NMR (C_6D_6) δ 42.55 (^1J(^{183}W–^{31}P) = 239 Hz); ^{1}H NMR (C_6D_6) δ 1.35 (s, CH$_3$), 3.57 (d, ^2J(H–P) = 9.4 Hz, PC*H*Ph), 5.97 (d, ^2J(H–P) = 23.9 Hz, PC*H*=), 7.0–7.4 (m, Ph); ^{13}C NMR (C_6D_6) δ 18.63 (d, ^3J(C–P) = 15.6 Hz, CH$_3$), 56.67 (d, ^1J(C–P) = 32.7 Hz, PCHPh), 158.01 (d, ^2J(C–P) = 7.5 Hz, =*C*CH$_3$), 196.30 (d, ^2J(C–P) = 7.04 Hz, cis CO), 199.44 (d, ^2J(C–P) = 23.7 Hz, trans CO); IR (Decalin) ν(CO) 2070 (m), 1950 (s), 1940 (vs) cm^{-1}; mass spectrum (^{184}W), *m*/*e* (rel intensity) 562 (M, 19), 478 (M – 3CO, 68), 422 (M – 5CO, 100). Anal. Calcd for $C_{21}H_{15}O_5PW$: C, 44.87; H, 2.69. Found: C, 45.46; H, 2.62.

5: yield 0.37 g (69%); colorless oil; ^{31}P NMR (pentane) δ 74.39 (^1J(^{183}W–^{31}P) = 239 Hz); ^{1}H NMR (C_6D_6) δ 0.96 (d, ^3J(H–P) = 14.7 Hz, C(CH$_3$)$_3$), 1.45 (d, br, ^4J(H–H) = 1.2 Hz, CH$_3$), 3.54 (d, ^2J(H–P) = 8.4 Hz, PC*H*Ph), 5.59 (dq, br, ^2J(H–P) = 23.8 Hz, ^4J(H–H) = 1.2 Hz, =CH), 6.9–7.2 (m, Ph); ^{13}C NMR (C_6D_6) δ 18.13 (d, ^3J(C–P) = 13.6, =C*C*H$_3$), 26.41 (d, ^2J(C–P) = 6.0 Hz, C(*C*H$_3$)$_3$), 35.33 (d, ^1J(C–P) = 6.0 Hz, P*C*(CH$_3$)$_3$), 49.46 (d, ^1J(C–P)= 29.7 Hz, P*C*HPh), 156.32 (d, ^2J(C–P) = 7.5 Hz, =*C*CH$_3$), 196.88 (d, ^2J(C–P) = 7.0 Hz, cis CO), 198.99 (d, ^2J(C–P) = 23.7 Hz, trans CO); IR (Decalin) ν(CO) 2070 (m), 1948 (s), 1950 (sh), 1944 (vs) cm^{-1}; mass spectrum (^{184}W), *m*/*e* (rel intensity) 542 (M, 15), 458 (M – 3CO, 47), 401 (M – C$_4$H$_9$ – 3CO, 64), 373 (M – C$_4$H$_9$ – 4CO, 53), 345 (M – C$_4$H$_9$ – 5CO, 100). Anal. Calcd for $C_{19}H_{19}O_5PW$: C, 42.09; H, 3.53. Found: C, 43.40; H, 3.65.

[4 + 2] Cycloadditions of Phosphabutadiene Complexes with 2,3-Dimethyl-1,3-butadiene (Reactions 6 and 7). Reaction 6: nBuLi (0.7 mL, 1.6 M solution in hexane) was added at –78 °C to a solution of complex **1** (0.57 g, 1 mmol) in THF. After a few minutes 2,3-dimethyl-1,3-butadiene (1.1 mL, 10 mmol) was added. 3,3-Dimethylacrylaldehyde (0.3 mL, 3 mmol) was then added, and the reaction mixture allowed to warm to room temperature. After hydrolysis and extraction with ether the final product was purified by chromatography with hexane/ether (99:1).

6: yield 0.34 g (59%); colorless solid, mp 74 °C (pentane); ^{31}P NMR (hexane) δ –10.66 (^1J(^{183}W–^{31}P) = 243 Hz); ^{1}H NMR (C_6D_6) δ 1.29 (d, *J*(H–P) = 6.0 Hz, CH$_3$), 1.30 (s, CH$_3$), 1.56 (s, CH$_3$), 1.65 (d, *J*(H–P) = 4.5 Hz, CH$_3$), 1.9 (m, 2 H), 2.50 (*A*B, *J*(H$_A$–H$_B$) = 17.2 Hz, 1 H (PCH$_2$)), 2.6–2.9 (m, 2 H, PC*H* + A*B* (PCH$_2$)), 5.25 (t, ^3J(H–H) ≃ ^3J(H–P) = 9.1 Hz, =CH), 6.9–7.3 (m, Ph); ^{13}C NMR (C_6D_6) δ 18.22 (s, CH$_3$), 20.00 (s, CH$_3$), 21.56 (d, ^3J(C–P) = 7.5 Hz, CH$_3$), 26.01 (s, CH$_3$), 32.30 (d, ^1J(C–P) = 24.7 Hz, PCH$_2$), 37.17 (d, ^1J(C–P) = 24.2 Hz, PCH), 37.20 (s, CH$_2$), 120.98 (d, *J*(C–P) = 4.5 Hz), 122.86 (s), 197.3 (d, ^2J(C–P) = 6.5 Hz, cis CO), 199.28 (d, ^2J(C–P) = 21.6 Hz, trans CO); IR (Decalin) ν(CO) 2070 (m), 1940 (vs) cm^{-1}; mass spectrum (^{184}W), *m*/*e* (rel intensity) 582 (M, 36), 498 (M – 3CO, 40), 470 (M – 4CO, 47), 442 (M – 5CO, 100). Anal. Calcd for $C_{22}H_{23}O_5PW$: C, 45.38; H, 3.98. Found: C, 45.46; H, 4.10.

Reaction 7: The same procedure as for (**6**) was used, with a cis/trans citral mixture (0.68 mL, 4 mmol) replacing 3,3-dimethylacrylaldehyde.

7: yield 0.58 g (89%); colorless oil; mixture of two isomers (cis/trans); ^{31}P NMR (hexane) δ –11.49 (^1J(^{183}W–^{31}P) = 243 Hz) and –11.11 (^1J(^{183}W–^{31}P) = 243 Hz), respectively (2:1 ratio); mass spectrum (^{184}W), *m*/*e* (rel intensity) 650 (M, 19), 566 (M – 3CO, 23), 538 (M – 4CO, 32), 508 (M – 5CO – 2, 100). ^{1}H NMR and ^{13}C NMR are in agreement with the proposed structure **7**.

Reactions of Complexes 1 and 2 with η^2-Fe(CO)$_4$ Complexes of α,β-Unsaturated Aldehydes (Reaction 8). (*trans*-Cinnamaldehyde)Fe(CO)$_4$, (crotonaldehyde)Fe(CO)$_4$, and (3-(2-furyl)acrolein)Fe(CO)$_4$ complexes are prepared as usual from diiron nonacarbonyl and the corresponding aldehyde in benzene at 40 °C (see, for example, ref 16).

(a) Synthesis of Complexes 8 and 9. nBuLi (0.7 mL, 1.6 M solution in hexane) was added at –78 °C to a solution of complex **1** (0.57 g, 1.0 mmol) in THF. After a few minutes a solution of the (cinnamaldehyde)Fe(CO)$_4$ complex (0.3 g, 1 mmol) in THF was added. The solution was allowed to warm to room temperature and stirred for about 1 h. After hydrolysis and evaporation, the final products were separated by chromatography. Complex **8** was eluted with hexane/ether (98:2); complex **9** was eluted with hexane/ether (95:5).

8: yield 0.30 g (43%); yellow–orange solid, mp 130 °C (pentane); ^{31}P NMR (C_6D_6) δ –37.38 (^1J(^{183}W–^{31}P) = 239 Hz); ^{1}H NMR (C_6D_6) δ 4.4 (m, ^3J(H–H) = 5.1 Hz, ^3J(H–H) = 6.4 Hz, ^3J(H–P) = 0 Hz (not resolved), 1 H, P–C*H*), 6.6–7.5 (m, Ph + C*H*=C*H*Ph); ^{13}C NMR (C_6D_6) δ 51.50 (d, ^1J(C–P) = 11.1 Hz, PCH), 131.15 (d, *J*(C–P) = 15.1 Hz, CH=), 133.25 (d, *J*(C–P) = 9.6 Hz, CH=), 137.06 (s, C(Ph)), 144.94 (d, ^1J(C–P) = 20.6 Hz, PC(Ph)), 197.19

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(16) Weiss, E.; Stark, K.; Lancaster, J. E.; Murdock, H. D. *Helv. Chim. Acta* **1963**, *27*, 288.

(d, ^{2}J(C–P) = 7.0 Hz, cis CO), 199.07 (d, ^{2}J(C–P) = 27.4 Hz, trans CO), 204.72 (s, br, Fe(*C*O)$_4$); IR (Decalin) ν(Fe(CO)$_4$) 2100 (m), 2042 (m), 2034 (s), 2010 (m), ν(W(CO)$_5$) 2070 (m), 1945 (vs), 1940 (sh) cm^{-1}; mass spectrum (^{184}W), *m/e* (rel intensity) 687 (M – CO – 1, 9), 660 (M – 2CO, 19), 632 (M – 3CO, 36), 576 (M – 5CO, 74), 548 (M)– "6CO", 80), 520 (M – "7CO", 85), 464 (M – "9CO", 100). Anal. Calcd for $C_{24}H_{13}O_9PWFe$: C, 40.26; H, 1.83. Found: C, 40.29; H, 2.00.

9: yield 0.14 g (20%); yellow–orange solid, mp 181 °C (pentane); ^{31}P NMR (C_6D_6) –30.61 (^{1}J(^{183}W–^{31}P) = 232 Hz); ^{1}H NMR (C_6D_6) δ 3.39 (d, ^{3}J(H–H) = 9.8 Hz, C*H*Ph), 4.96 (d, ^{3}J(H–H) = 6.1 Hz, PC*H*), 5.74 (m, ^{3}J(H–P) = 21.5 Hz, ^{3}J(H–H) = 9.8 Hz, ^{3}J(H–H) = 6.1 Hz, C*H*CHPh), 6.9–7.3 (m, Ph); ^{13}C NMR (C_6D_6) δ 68.30 (d, *J*(C–P) = 20.2 Hz), 75.98 (d, *J*(C–P) = 14.6 Hz), 89.98 (d, *J*(C–P) = 8.1 Hz,), 136.70 (s, C(Ph)), 140.75 (d, ^{1}J(C–P) = 24.2 Hz, PC(Ph)), 195.77 (d, ^{2}J(C–P) = 6.5 Hz, cis CO), 198.32 (d, ^{2}J(C–P) = 29.2 Hz, trans CO), 207.57 (very br and w, Fe(*C*O)$_3$); IR (Decalin) ν(Fe(CO)$_3$) 2052 (s), 2008 (m), 1982 (w), ν(W(CO)$_5$) 2070 (w), 1948 (vs), 1940 (sh) cm^{-1}; mass spectrum (^{184}W), *m/e* (rel intensity) 660 (M – CO, 8), 632 (M – 2CO, 13), 576 (M – 4CO, 28), 548 (M – "5CO", 43), 520 (M – "6CO", 28), 492 (M – "7CO", 19), 464 (M – "8CO", 100). Anal. Calcd for $C_{23}H_{13}O_8PWFe$: C, 40.15; H, 1.90. Found: C, 41.78; H, 2.11.

(b) Synthesis of Complexes 10 and 11. The same procedure as for (a) was used with complex **2** (0.55 g, 1.0 mmol) replacing complex **1** as starting material. The reaction mixture was left at room temperture for about 20 min, and after chromatography with hexane/ether (98:2) a mixture of **10** and **11** was obtained (8:2 ratio), total yield 42%.

10 and **11** were separated by crystallization from a pentane/ether solution; the major product **10** was obtained in the pure state, and **11** was obtained then by crystallization of the residue from pentane.

10: yellow–orange solid, mp 131 °C; ^{31}P NMR (C_6D_6) δ 8.98 (^{1}J(^{183}W–^{31}P) = 234 Hz); ^{1}H NMR (C_6D_6) δ 0.93 (d, ^{3}J(H–P) = 16.2 Hz, C(C*H*$_3$)$_3$), 4.42 (dd, ^{3}J(H–P) ≃ 0 Hz, ^{3}J(H–H) = 10.0 Hz, ^{3}J(H–H) = 4.7 Hz, PC*H*), 6.6–7.4 (m, Ph + C*H*=C*H*Ph); ^{13}C NMR (C_6D_6) δ 30.13 (d, ^{2}J(C–P) = 7.0 Hz, C(*C*H$_3$)$_3$), 37.32 (s, *C*(CH$_3$)$_3$), 54.15 (d, ^{1}J(C–P) = 24.7 Hz, PCH), 130.82 (d, *J*(C–P) = 13.6 Hz, CH=), 134.54 (d, *J*(C–P) = 5.5 Hz, CH=), 137.25 (s, C(Ph)), 198.81 (d, ^{2}J(C–P) = 7.5 Hz, cis CO), 206.16 (s, Fe(*C*O)$_4$); IR (Decalin) ν(Fe(CO)$_4$) 2090 (m), 2050 (w), 2035 (m), 2012 (s), ν(W(CO)$_5$) 2065 (m), 2045 (vs), 2030 (vs) cm^{-1}; mass spectrum (^{184}W), *m/e* (rel intensity) 640 (M – 2CO, 9), 612 (M – 3CO, 9), 556 (M – 5CO, 20), 528 (M – "6CO", 38), 500 (M – "7CO", 21), 444 (M – "9CO", 28), 416 (M – Fe – 8CO, 34), 388 (M – Fe – 9CO, 100). Anal. Calcd for $C_{22}H_{17}O_9PWFe$: C, 37.96; H, 2.46. Found: C, 38.49; H, 2.41. These poor results are due to the low stability of the product upon standing.

11: yellow–orange solid, mp 166 °C (dec); ^{31}P NMR (C_6D_6) δ 13.50 (^{1}J(^{183}W–^{31}P) = 227 Hz); ^{1}H NMR (C_6D_6) δ 1.02 (d, ^{3}J(H–P) = 15.3 Hz, C(C*H*$_3$)$_3$), 3.74 (d, ^{3}J(H–H) = 10.4 Hz, C*H*Ph), 4.80 (d, ^{3}J(H–H) = 6.9 Hz, PC*H*), 5.62 (m, ^{3}J(H–P) = 19.4 Hz, ^{3}J(H–H) = 10.4 Hz, ^{3}J(H–H) = 6.9 Hz, C*H*CHPh), 6.9–7.4 (m, Ph); ^{13}C NMR (C_6D_6) δ 31.00 (d, ^{2}J(C–P) = 6.0 Hz, C(*C*H$_3$)$_3$), 36.92 (s, *C*(CH$_3$)$_3$), 69.38 (d, *J*(C–P) = 15.6 Hz), 82.12 (d, *J*(C–P) = 27.2 Hz, 88.72 (d, *J*(C–P), not resolved), 137.48 (s, C(Ph)), 197.50 (d, ^{2}J(C–P) = 6.5 Hz, cis CO), 208.90 (s, Fe(*C*O)$_3$); IR (Decalin) ν(Fe(CO)$_3$) 2052 (s), 2007 (m), 1980 (m), ν(W(CO)$_5$) 2072 (w), 1940 (vs) cm^{-1}; mass spectrum (^{184}W), *m/e* (rel intensity) 640 (M – CO, 5), 556 (M – 4CO, 10), 528 (M – "5CO", 23), 444 (M – "8CO", 13), 416 (M – Fe – 7CO, 17), 388 (M – Fe – 8CO, 30), 288 (LFe(CO), 40), 260 (LFe, 62), 204 (tBuP=CH—CH=CHPh, 100). Anal. Calcd for $C_{21}H_{17}O_8PWFe$: C, 37.76; H, 2.57. Found: C, 37.84; H, 2.51.

(c) Synthesis of Complex 13. The same procedure as for (a) was used with (crotonaldehyde)Fe(CO)$_4$ complex (0.24 g, 1.0 mmol) replacing the (cinnamaldehyde)Fe(CO)$_4$ complex. The reaction mixture was stirred at room temperature for 1.5 h. After chromatography with hexane/ether (98:2), complex **13** was obtained in 25% yield (0.16 g).

13: yellow–orange solid, mp 116 °C (pentane); ^{31}P NMR (C_6D_6) δ –27.52 (^{1}J(^{183}W–^{31}P) = 232 Hz); ^{1}H NMR (C_6D_6) δ 1.19 (d, ^{3}J(H–H) = 6.2 Hz, CH$_3$), 2.15 (dq, ^{3}J(H–H) = 8.5 Hz, ^{3}J(H–H) = 6.2 Hz, C*H*CH$_3$), 4.7 (m, 2 H, PC*H*C*H*), 6.9–7.2 (m, Ph); ^{13}C NMR (C_6D_6) δ 18.86 (s, CH$_3$), 66.91 (d, *J*(C–P) = 19.6 Hz), 76.65 (d, *J*(C–P) = 14.1 Hz), 96.52 (d, *J*(C–P) = 8.1 Hz), 141.80 (d, ^{1}J(C–P) = 24.2 Hz, P*C*(Ph)), 196.73 (d, ^{2}J(C–P) = 6.0 Hz, cis CO), 198.66 (d, ^{2}J(C–P) = 28.7 Hz, trans CO), 208.86 (br, Fe(*C*O)$_3$); IR (Decalin) ν(Fe(CO)$_3$) 2055 (s), 2006 (s), 1998 (s), ν(W(CO)$_5$) 2070 (m), 1945 (vs) cm^{-1}; mass spectrum (^{184}W), *m/e* (rel intensity) 626 (M, 6), 598 (M – CO, 15), 570 (M – 2CO, 23), 486 (M – "5CO", 64), 402 (M – 8CO, 100). Anal. Calcd for $C_{18}H_{11}O_8PWFe$: C, 34.54; H, 1.77. Found: C, 33.94; H, 1.89.

(d) Synthesis of Complexes 14 and 15. The same procedure as for (c) was used with complex **2** (0.55 g, 1.0 mmol) replacing **1**. The reaction mixture was stirred at room temperature for 20 min. Chromatography with hexane/ether (97:3) yields 0.33 g (54%) of a 1:1 mixture of complexes **14** and **15** (ratio obtained by ^{31}P NMR spectroscopy) [**14**: ^{31}P NMR (hexane/ether) δ 6.42 (^{1}J(^{183}W–^{31}P) = 239 Hz)]. The mixture of complexes **14** and **15** was heated at 80 °C in benzene for 40 min.[17] Pure **15** was obtained by chromatography with hexane/ether (97:3).

15: yield 0.24 g (40%); yellow–orange solid, mp 91 °C (pentane); ^{31}P NMR (C_6D_6) δ 17.56 (^{1}J(^{183}W–^{31}P) = 225 Hz); ^{1}H NMR (C_6D_6) δ 0.97 (d, ^{3}J(H–P) = 15.3 Hz, C(C*H*$_3$)$_3$), 1.21 (d, ^{3}J(H–H) = 6.3 Hz, CHC*H*$_3$), 2.41 (dq, ^{3} *J*(H–H) = 9.6 Hz, ^{3}J(H–H) = 6.3 Hz, C*H*CH$_3$), 4.58 (*A*B, ^{3}J(H$_A$–H$_B$) = 6.6 Hz, PC*H*), 4.78 (m, ^{3}J(H–P) = 19.6 Hz, ^{3}J(H–H) = 9.7 Hz, ^{3}J(H$_A$–H$_B$) = 6.6 Hz, C*H*CHMe); ^{13}C NMR (C_6D_6) δ 18.39 (s, CH*C*H$_3$), 30.96 (d, ^{2}J(C–P) = 6.0 Hz, C(*C*H$_3$)$_3$), 36.67, (s, *C*(CH$_3$)$_3$), 67.00 (d, *J*(C–P) = 16.6 Hz), 81.76 (d, *J*(C–P) = 26.2 Hz), 94.27 (d, *J*(C–P) = 5.5 Hz), 197.58 (d, ^{2}J(C–P) = 6.5 Hz, cis CO), 209.49 (s, Fe(*C*O)$_3$); IR (Decalin) ν(Fe(CO)$_3$) 2050 (s), 2002 (s), 1984 (s), ν(W(CO)$_5$) 2070 (m), 1940 (vs) cm^{-1}; mass spectrum (^{184}W), *m/e* (rel intensity) 578 (M – CO, 13), 550 (M – 2CO, 23), 552 (M – 3CO, 21), 494 (M – 4CO, 38), 466 (M – "5CO", 21), 438 (M – "6CO", 100). Anal. Calcd for $C_{16}H_{15}O_8PWFe$: C, 31.71; H, 2.50. Found: C, 31.73; H, 2.39.

(e) Synthesis of Complexes 16 and 17. The same procedure as for (a) was used with (3-(2-furyl)acrolein)Fe(CO)$_4$ (0.30 g, 1.0 mmol) replacing the (cinnamaldehyde)Fe(CO)$_4$ complex. After 30 min of stirring at room temperature, the mixture of **16** and **17** was purified by chromatography with hexane/ether (90:10), yield 0.31 g (45%) [**16**: ^{31}P NMR (hexane/ether) δ –35.65 (^{1}J(^{183}W–^{31}P) = 239 Hz)]. The mixture of complexes **16** and **17** was heated for 3 h in refluxing benzene to convert **16** into **17**.

17: yellow solid; ^{31}P NMR (pentane/ether) δ –26.84 (^{1}J(^{183}W–^{31}P) = 234 Hz); ^{1}H NMR (C_6D_6) δ 3.38 (d, ^{3}J(H–H) = 9.8 Hz, C*H*–furyl), 4.83 (d, ^{3}J(H–H) = 6.5 Hz, PC*H*), 5.84 (m, ^{3}J(H–P) = 22.0 Hz, ^{3}J(H–H) = 9.8 Hz, ^{3}J(H–H) = 6.5 Hz, PCHC*H*), 5.93 (m, 1 H, furyl), 6.25 (d, ^{3}J(H–H) = 3.3 Hz, 1 H, furyl), 6.8–7.2 (m, Ph + 1 H, furyl); ^{13}C NMR (C_6D_6) δ 61.13 (d, *J*(C–P) = 21.1 Hz), 76.38 (d, *J*(C–P) = 14.1 Hz), 88.60 (d, *J*(C–P) = 8.6 Hz), 109.21 (s, CH, furyl), 112.56 (s, CH, furyl, 142.71 (s), 152.58 (s), 196.66 (d, ^{2}J(C–P) = 7.0 Hz, cis CO); IR (Decalin) ν(Fe(CO)$_3$) 2060 (s), 2015 (m), 1987 (w), ν(W(CO)$_5$) 2070 (w), 1950 (vs), 1945 (sh) cm^{-1}; mass spectrum (^{184}W), *m/e* (rel intensity) 677 (M – 1, 13), 650 (M – CO, 28), 594 (M – 3CO, 30), 538 (M – "5CO", 51), 510 (M – "6CO", 68), 482 (M – "7CO", 53), 454 (M – "8CO", 100).

(f) Synthesis of Complexes 18 and 19. The same procedure as for (e) was used, with complex **2** (0.55 g, 1.0 mmol) replacing **1** as starting material. After 1 h at room temperature, the reaction mixture was chromatographed with ether. A mixture of **18** and **19** was thus obtained [**18**: ^{31}P NMR (ether) δ 9.96]. The mixture was heated in refluxing benzene for 2 h to convert **18** into **19**. Chromatography with hexane/ether (94:6) yields pure **19**.

19: yield 0.24 g (36%); yellow solid, mp 160 °C (dec); ^{31}P NMR (C_6D_6) δ 15.15 (^{1}J(^{183}W–^{31}P) = 227 Hz); ^{1}H NMR (C_6D_6) δ 0.99 (d, ^{3}J(H–P) = 7.8 Hz, C(C*H*$_3$)$_3$), 3.73 (d, ^{3}J(H–H) = 9.9 Hz, C*H*–furyl), 4.68 (d, ^{3}J(H–H) = 6.8 Hz, PC*H*), 5.77 m, ^{3}J(H–P) = 19.8 Hz, ^{3}J(H–H) = 9.9 Hz, ^{3}J(H–H) = 6.8 Hz, PCHC*H*), 5.92 (m, 1 H (furyl)), 6.22 (d, ^{3}J(H–H) = 3.3 Hz, 1 H (furyl), 6.92 (s, br, 1 H, furyl); ^{13}C NMR (C_6D_6) δ 31.02 (d, ^{2}J(C–P) = 6.0 Hz, C(*C*H$_3$)$_3$), 36.89 (s, *C*(CH$_3$)$_3$), 75.58 (d, *J*(C–P) = 17.1 Hz), 81.67 (d, *J*(C–P) = 26.7 Hz), 86.44 (d, not resolved), 109.48 (s, CH, furyl), 112.57 (s, CH, furyl), 142.79 (s, CH, furyl), 152.28 (s, *C*, furyl), 197.55 (d, ^{2}J(C–P) = 6.0 Hz, cis CO), 208.74 (s, Fe(*C*O)$_3$); IR (Decalin) ν(Fe(CO)$_3$) 2068 (s), 2013 (s), 1985 (s), ν(W(CO)$_5$) 2075 (m), 1944 (vs) cm^{-1}; mass spectrum (^{184}W), *m/e* (rel intensity) 658

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(17) A pure sample of complex **8** is quantitatively converted to **9** when heated for 6 h at 70 °C in benzene solution.

(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 = 0.71073 Å), graphite monochromator, μ = 65.0 cm^{-1}, $F(000)$ = 1156. A total of 6539 unique reflexions were recorded in the range 2° ≤ 2θ ≤ 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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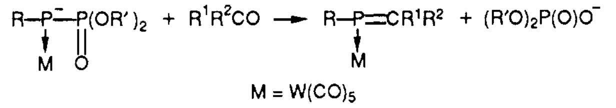
The so-called "phospha-Wittig" reagents $[(EtO)_2P(O)PHR]M(CO)_5$ (M = Mo, W) are obtained via the reaction of primary phosphine complexes $(RPH_2)M(CO)_5$ with lithium diisopropylamide and diethyl chlorophosphate. The corresponding anions $[(EtO)_2P(O){-}P^{-}R]M(CO)_5$ react with carbonyl compounds 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:



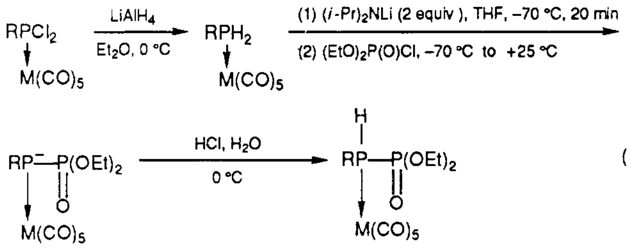
$$\underset{\downarrow\atop M}{R{-}P^{-}}{-}\underset{\|\atop O}{P}(OR')_2 + R^1R^2CO \longrightarrow R{-}\underset{\downarrow\atop M}{P}{=}CR^1R^2 + (R'O)_2P(O)O^-$$

M = W(CO)$_5$

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-



(1)

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%

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[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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