added slowly to a stirred solution of (η^5-chlorodivinylborane)cyclopentadienylcobalt (0.4135 g, 1.84 mmol) in 20 mL of ether. The resulting mixture was stirred at room temperature for 1 h. The resulting solution was filtered over a short plug of alumina (7% H_2O) (2 × 3 cm). The solvent was removed from the filtrate under high vacuum. The residual oil was extracted with a minimum amount of pentane and the resulting solution slowly cooled to −78 °C to give a red crystalline solid. The solvent was decanted, and the crystals melted as the sample was allowed to warm to room temperature under high vacuum to give (η^5-phenyldivinylborane)cyclopentadienylcobalt, 0.4541 g (93%), as a red oil.

Anal. Calcd for $C_{15}H_{16}BCo$: C, 67.72; H, 6.06. Found: C, 67.21; H, 5.86.

(η^5-Divinylborane)cyclopentadienylcobalt (8). To a stirred solution of (η^5-chlorodivinylborane)cyclopentadienylcobalt (0.8084 g, 3.60 mmol) in 50 mL of ether at 0 °C was added slowly solid $LiBH_4$ (0.2010 g, 9.26 mmol). The resulting mixture was allowed to warm to room temperature, followed by continued stirring for 2 h. The reaction mixture was diluted with 50 mL of hexane and filtered over a column of silica gel (2 × 5 cm). The silica gel column was washed with 20 mL of hexane and the combined ether-hexane solution concentrated under vacuum to $\simeq$20 mL. The resulting solution was cooled slowly to −78 °C to give, upon filtration and drying under high vacuum, 0.4361 g of (η^5-divinylborane)cyclopentadienylcobalt. The mother liquor was further concentrated to 5 mL to produce a second crop of product, 0.1318 g, to give a combined yield of 0.5679 g (70%); mp 83 °C.

Anal. Calcd for $C_9H_{12}BCo$: C, 56.71; H, 6.37. Found: C, 56.84; H, 6.48.

Acknowledgment. I wish to thank Prof. G. E. Herberich for his help in carrying out this work.

Registry No. 1, 73939-32-9; 2, 114860-71-8; 3, 114860-72-9; 4, 11486-73-0; 5, 114860-74-1; 6, 114860-75-2; 7, 114860-76-3; 8, 114860-77-4; 3,5-dichlorobenzyl alcohol, 60211-57-6.

Synthesis of the Phosphorus–Carbon Double Bond by Reaction between Pentacarbonylchromium or -tungsten Complexes of Phosphinidenes and Carbenes. Application to the Synthesis of the 1,2-Dihydrophosphete Ring

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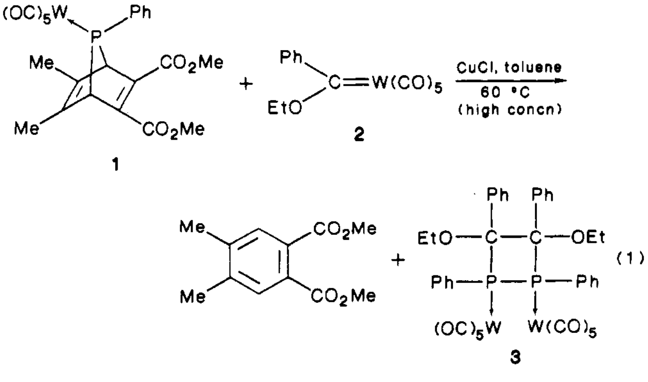
Received December 21, 1987

The condensation of a carbene complex $R^1R^2C{=}M(CO)_5$ with a transient terminal phosphinidene complex $[RP{=}M(CO)_5]$ (M = Cr, W) primarily yields a phosphaalkene complex, $R^1R^2C{=}P(R){\rightarrow}M(CO)_5$, which, in some cases, dimerizes. This method has been applied to the synthesis of $Ph_2C{=}P(Ph){\rightarrow}W(CO)_5$ which is stable as a monomer. When a vinylcarbene complex such as $PhCH{=}CH{-}C(OEt){=}Cr(CO)_5$ is reacted with (phenylphosphinidene)pentacarbonyltungsten, the transient phosphabutadiene complex thus obtained instantly undergoes a [2 + 2] cyclization to give a (1,2-dihydrophosphete(*P*–*W*))pentacarbonyltungsten complex. The X-ray crystal structure analysis of this complex [$C_{22}H_{17}O_6PW$, fw 592.20; space group $P\bar{1}$ (No. 2) with a = 10.519 (1) Å, b = 10.887 (1) Å, c = 11.134 (1) Å, α = 112.78 (2)°, β = 98.15 (2)°, γ = 97.13 (2)°; V = 1141.18 (68) Å^3; Z = 2; d(calcd) = 1.723 g cm^{-3}] confirms the presence of the four-membered ring with a very long P–C sp^3-intracyclic bond [1.902 (5) Å]. It proved possible to convert this complex into the corresponding *P*-oxide without breaking the ring.

Recently we have shown on a preliminary example[1] that it is possible to couple a phosphinidene and a carbene to get a P=C double bond via the reaction of a transient terminal phosphinidene complex with a carbene complex. In view of the synthetic potential of this new approach to phosphaalkenes, we decided to explore a little bit further this reaction in order to check some points of its postulated mechanism, to extend its scope, and to show on a precise example what kind of applications can be built around it.

Results and Discussion



In our preliminary experiment,[1] we allowed the 7-phosphanorbornadiene complex 1 to react with the carbene complex 2 (eq 1). The final product was the 1,2-diphosphetane complex 3. The postulated mechanism is depicted in eq 2. In this mechanism, the copper(I) chloride only plays the role of a catalyst which promotes the decomposition of the phosphinidene precursor 1[2] but does not in-

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(1) Tran Huy, N. H.; Mathey, F. *Organometallics* **1987**, *9*, 207.

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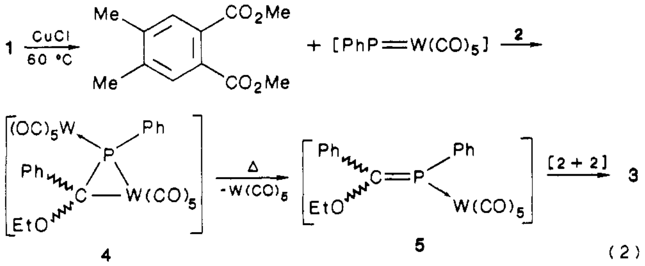
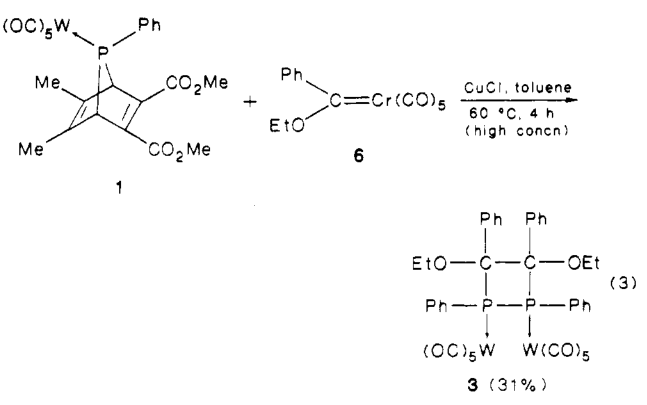
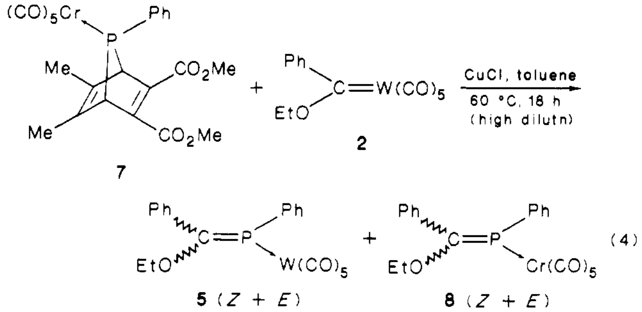


4 5 (2)

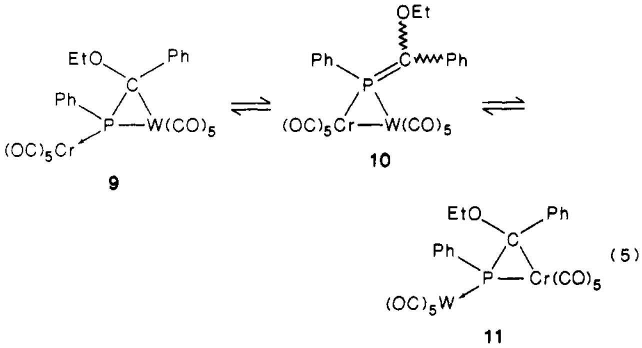
terfere with the phosphinidene–carbene coupling itself. In order to check this scheme, we performed three experiments. In the first one, we simply repeated the same reaction (eq 1) with the minimum acceptable amount of CuCl to keep the decomposition temperature of 1 sufficiently low and with a high dilution of the reagents. In so doing, we were able to isolate the phosphaalkene complex 5 as a mixture of the *Z* and *E* isomers. This mixture gives two ^{31}P resonances at low fields: $\delta(^{31}P)$ +105.1 and +126.6 (major) in toluene. Its mass spectrum (EI, 70 eV, ^{184}W) confirms the formula: *m/z* (relative intensity) 566 (M, 32), 426 (M − 5CO, 76), 367 (100). When 5 in toluene was heated with CuCl, it slowly disappeared to give the dimer 3 (without CuCl, the dimerization is more difficult). Thus, this experiment clearly demonstrates that the normal end product of the condensation of a phosphinidene with a carbene complex is indeed a phosphaalkene complex. In the second experiment, the phosphinidene precursor 1 was heated with the chromium–carbene complex 6 by using the same experimental conditions as in our previous note.[1] In so doing, we obtained the 1,2-diphosphetane complex 3 (eq 3). This experiment confirms that, during the condensation process, the metal of the carbenic complex is preferentially lost as proposed in the mechanism depicted in eq 2. However, in some instances, some scrambling may occur between the metals of the phosphinidene and carbene complexes. Indeed, when the precursor of the (phenylphosphinidene)pentacarbonylchromium complex 7 was heated with the tungsten–carbene complex 2, only chromium–phosphaalkene complexes would be expected according to the postulated mechanism. In fact, we obtained a mixture of chromium- and tungsten–phosphaalkene complexes 8 and 5, respectively (eq 4). Indeed, the ^{31}P NMR spectrum of the crude reaction product showed the two resonances expected for 5 at 101.5 and 123.5 ppm (in CH_2Cl_2) together with two other resonances at 146.6 and 170.7 ppm which could correspond to 8. The mass spectrum of the same mixture (EI, 70 eV, ^{184}W) was also informative: *m/z* (relative intensity) 566 [M (5), 6.6], 434 [M (8), 12.3], 426 [M (5) − 5CO, 15.3], 294 [M (8) − 5CO, 100]. This result suggests that some exchange can take place between the two metals of the intermediate σ,π-complex 9. We propose a mechanism involving a μ_2-phosphaalkene complex, 10, similar to those described by Scherer with $R_2N{-}P{=}NR'$[3] (eq 5).



1 6 3 (31%) (3)

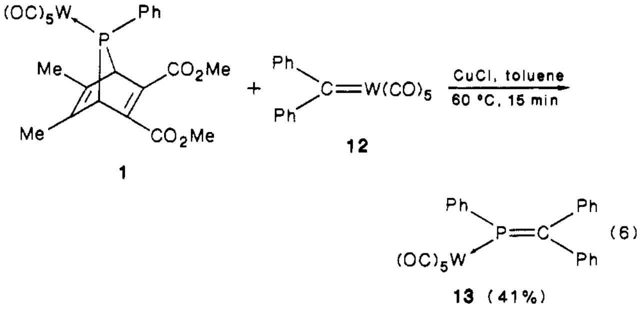


7 2 5 (*Z* + *E*) 8 (*Z* + *E*) (4)



9 10 11 (5)

In order now to get a preliminary idea of the scope of this new synthesis of the P═C double bond, we chose to study the reaction between the phosphinidene precursor 1 and the (diphenylcarbene)tungsten complex 12.[4] This reaction gave the expected phosphaalkene complex 13 (eq 6). The low-field shift of the ^{31}P resonance of 13 ($\delta(^{31}P)$ +187 in CH_2Cl_2) confirms the presence of a P═C double bond. The P═*C* carbon appears at +186.7 ppm with a $^{1}J(P{=}C)$ coupling of 43.2 Hz. These data are also very characteristic of a P═C double bond.[5] The mass spectrum (EI, 70 eV, ^{184}W) confirms the formula: *m/z* (relative intensity) 598 (M, 13), 514 (M − 3CO, 40), 458 (M − 5CO, 87), 456 (100). It is interesting to note that the diphenylcarbene complex reacts far more rapidly with 1 than



1 12 13 (41%) (6)

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[2] A recent review discusses the use of 7-phosphanorbornadiene complexes as precursors of transient terminal phosphinidene complexes; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275. More recently, it has been shown that it is possible to stabilize such phosphinidene complexes either as adducts with amines or by increasing the steric hindrance and reducing the electrophilicity of phosphorus: Cowley, A. H.; Geerts, R. L.; Nunn, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 6523. Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P. *J. Chem. Soc., Chem. Commun.* **1987**, 1282.

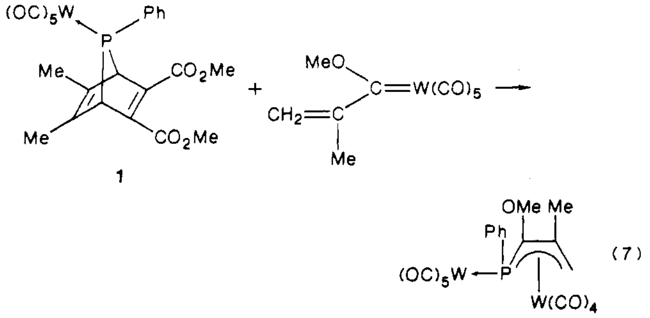
[3] Scherer, O. J.; Konrad, R.; Guggolz, E.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 297. See also: Holand, S.; Charrier, C.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1984**, *106*, 826.

[4] Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127.

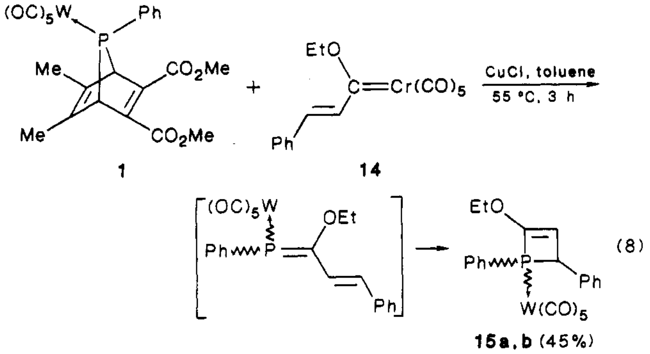
[5] Klebach, Th. C.; Lourens, R.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1978**, *100*, 4886.

the alkoxy-substituted carbene complexes. On the other hand, this experiment demonstrates once again that W$(CO)_5$ is able to stabilize an otherwise unstable phosphorus compound. Indeed, 1,2,2-triphenylphosphaethylene is unknown in the free state.[5]

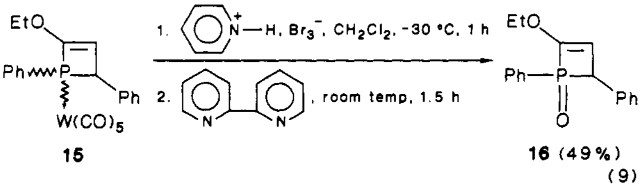
With this new synthesis of the P═C double bond in our hands, it seemed appropriate to illustrate its potential by a specific application in organophosphorus chemistry. In a previous note,[6] we had already shown that the reaction of the phosphinidene precursor 1 with a tungsten–vinylcarbene complex led to an original η^4-phosphabutadiene complex (eq 7). The various experiments reported here



(eq 3 and 4) suggest that the (η^2-P═C) chromium π-complexes are more labile than the corresponding tungsten complexes. Thus, we repeated the experiment of eq 7 with a chromium–vinylcarbene complex, 14.[7] In so doing, we hoped to obtain a free phosphabutadiene unit. In fact, this unit was transiently produced but immediately cyclized to give a 1,2-dihydrophosphete ring 15 as a mixture of two isomers (eq 8). The mass spectrum of 15 (EI, 70 eV, ^{184}W)

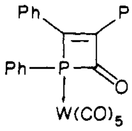


demonstrated that 15 had the same experimental formula as the expected phosphabutadiene: *m/z* (relative intensity) 592 (M, 34), 479 (M − 4CO − H, 100). However, the ^{31}P NMR spectrum ruled out a phosphabutadiene formulation: $\delta(^{31}P)$ 57.4 (major) and 61.1 (minor) in CH_2Cl_2. That the cyclization had taken place was clearly visible on the ^{13}C NMR spectrum that showed two sp^3 CHPh carbons at 45.13 (minor) and 46.38 (major) ppm which were both strongly coupled with phosphorus: ^1J(C–P) = 30.2 and 33.7 Hz, respectively. The cyclization was confirmed by a X-ray crystal structure analysis whose data are discussed below. Similar ring closures have been reported for 1,4-diphosphabutadienes by Appel,[8] and, very recently, Neilson has also shown that sterically protected 1-phosphabutadienes tend to cyclize upon oxidation at phosphorus.[9] At the moment, only four reports are available in the literature on the 1,2-dihydrophosphete ring.[9–11] The reports from our laboratory[11] in fact deal with 2-keto-1,2-dihydrophosphete derivatives in which the keto group interferes with the reactivity of the ring.[11b] The Russian report[10] is perhaps erroneous (this point is discussed in ref 11a). Thus we are left with the recent report of Neilson[9] in which bulky silyl substituents are used to impart some stability to the free 1-phosphabutadiene unit. In view of this situation, we thought that a preliminary study of 15 would be worthwhile. Our first aim was to check whether or not the complexation was necessary to impart some stability to a 1,2-dihydrophosphete ring without bulky substituents. For that purpose, we decided to decomplex the phosphorus atom of 15 using an already described procedure.[11a] We thus obtained the stable 1,2-dihydrophosphete *P*-oxide 16 (eq 9). The oxide 16 is



obtained as a mixture of two isomers, the most abundant of which can be recovered in the pure state by crystallization in pentane/CH_2Cl_2. The two most striking spectral characteristics of this product are the huge ^3J(H–P) coupling between the ethylenic proton on the ring and phosphorus (65.6 Hz) (this huge coupling has already been noted by Neilson[9b] on similar products) and the huge ^1J(C–P) coupling between the sp^3 ring carbon and phosphorus (58.2 Hz). This value is far higher than that reported for the same coupling in the 1,2-dihydrophosphete *P*-oxide described by the Russian authors[10] (18.3 Hz) and cast some doubt on their results.

Since the only 1,2-dihydrophosphete X-ray crystal structure reported in the literature concerned the 2-keto derivative 17[11a] and was not necessarily representative of


17

the normal geometry of this ring, we decided to perform the X-ray crystal structure analysis of 15. The most significant data are given in the caption of Figure 1. All in all, it can be stated that the geometry of the 1,2-dihydrophosphete ring is surprisingly similar in 15 and 17. For example, the strain at phosphorus as measured by the C_{ring}–P–C_{ring} intracyclic angle is almost identical: 15, 74.0 (2)°; 17, 71.9 (5)°. In both cases, the C═C double bond is well-localized: 15, 1.331 (7) Å; 17, 1.36 (1) Å. Indeed, the conjugation between the carbonyl and the C═C double bond in 17 remains minimal as indicated by the C_{ring}–C_{ring} single bond length: 15, 1.517 (7) Å; 17, 1.48 (1) Å. Even the ring distorsion induced by the keto group of 17 at the corresponding carbon is surprisingly negligible as monitored by the P–C_{ring}–C_{ring} angle: 15, 86.5 (3)°; 17, 88.8 (7)°. In both cases, the bond between the sp^3 ring carbon and phosphorus is very weak: 15, 1.902 (5) Å; 17, 1.93 (1) Å.

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(6) Tran Huy, N. H.; Fischer, J.; Mathey, F. *J. Am. Chem. Soc.* **1987**, *109*, 3475.

(7) Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537.

(8) Appel, R.; Barth, V. *Tetrahedron Lett.* **1980**, *21*, 1923.

(9) (a) Neilson, R. H.; Boyd, B. A.; Dubois, D. A.; Hani, R.; Scheide, G. M.; Shore, J. T.; Wettermark, U. G. *Phosphorus Sulfur* **1987**, *30*, 463. (b) Boyd, B. A.; Thoma, R. J.; Neilson, R. H. *Tetrahedron Lett.* **1987**, *28*, 6121.

(10) Nurtdinov, S. Kh.; Ismagilova, N. M.; Fakhrutdinova, R. A.; Zykova, J. V. *Zh. Obshch. Khim.* **1983**, *53*, 1045; *Chem. Abstr.* **1983**, *99*, 122548z.

(11) (a) Marinetti, A.; Fischer, J.; Mathey, F. *J. Am. Chem. Soc.* **1985**, *107*, 5001. (b) Marinetti, A.; Mathey, F. *Organometallics* **1988**, *7*, 633.

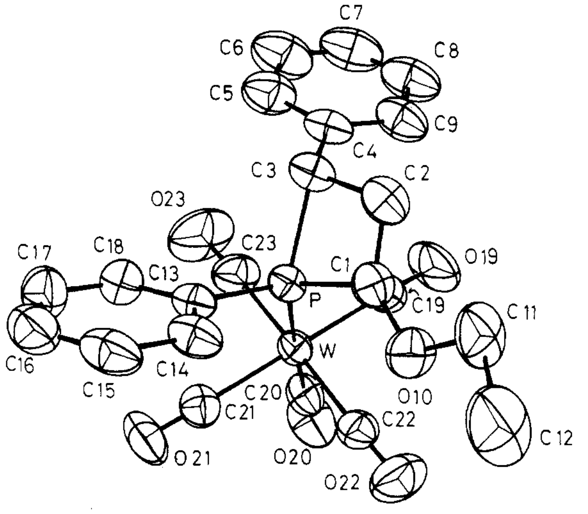
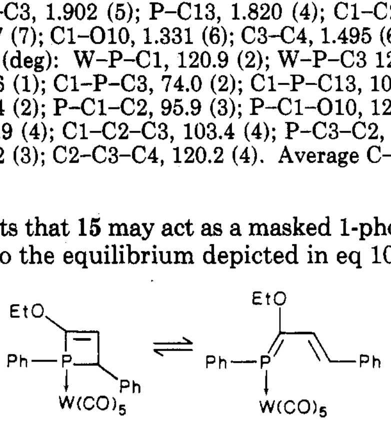


Figure 1. ORTEP representation of $C_{22}H_{17}O_6$ PW with thermal ellipsoids at the 50% probability level; hydrogen atoms are omitted. Principal bond distances (Å): W–P, 2.484 (1); P–C1, 1.815 (4); P–C3, 1.902 (5); P–C13, 1.820 (4); C1–C2, 1.331 (7); C2–C3, 1.517 (7); C1–O10, 1.331 (6); C3–C4, 1.495 (6). Selected bond angles (deg): W–P–C1, 120.9 (2); W–P–C3 125.6 (1); W–P–C13, 117.6 (1); C1–P–C3, 74.0 (2); C1–P–C13, 105.7 (2); C3–P–C13, 104.4 (2); P–C1–C2, 95.9 (3); P–C1–O10, 127.2 (3); C2–C1–O10 136.9 (4); C1–C2–C3, 103.4 (4); P–C3–C2, 86.5 (3); P–C3–C4, 119.2 (3); C2–C3–C4, 120.2 (4). Average C–H distance: 1.01 (15) Å.

This suggests that **15** may act as a masked 1-phosphadiene according to the equilibrium depicted in eq 10. Finally,



15

(10)

the ring of **15** is practically planar. The deviations from the mean ring plane are as follows: P, 0.0168 (11) Å; C_1, -0.0246 (46) Å; C_2, 0.0284 (51) Å; C_3, -0.0205 (46) Å.

Experimental Section

All reactions were carried out under dry oxygen-free argon atmosphere. All solvents were freshly distilled over appropriate drying agents. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker WP 80 spectrometer at 80.13, 20.15, and 32.435 MHz. Some ^{1}H and ^{13}C spectra were recorded on a Bruker 200-MHz ACSY instrument. Chemical shifts are given in parts per million downfield from internal Me_4Si for ^{1}H and ^{13}C shifts and from external 85% H_3PO_4 for ^{31}P shifts whereas coupling constants are given in hertz (Hz). Infrared spectra were recorded on a Perkin-Elmer 297 spectrophotometer and mass spectra on a Shimadzu GCMS-QP 1000 spectrometer at 70 eV.

Reaction of the 7-Phosphanorbornadiene Complex 1 with (Phenylethoxycarbene)pentacarbonyltungsten. A solution of the 7-phosphanorbornadiene complex 1 (6.8 g, 10.4 × 10^{-3} mol) and (phenylethoxycarbene)pentacarbonyltungsten (**2**) (4 g, 8.7 × 10^{-3} mol) in toluene (75 mL) was heated at 55–60 °C for 4.5 h with 100 mg of CuCl. The disappearance of the carbene complex was followed by TLC. After evaporation, the crude reaction product was chromatographed on Florisil at -10 °C with pentane. A mixture of the two isomers of **5** was thus obtained as a yellow oil (2 g, ca. 41%): ^{1}H NMR ($CDCl_3$) δ 1.04 and 1.28 (2t, 3 H, Me), 3.70 and 3.79 (2q, 2 H, OCH_2), 7.17 and 7.39 (2m, 10 H, Ph). See the Discussion for the ^{31}P NMR and mass spectra.

Reaction of the 7-Phosphanorbornadiene Complex 1 with (Phenylethoxycarbene)pentacarbonylchromium. A solution of the 7-phosphanorbornadiene complex 1 (2.3 g, 3.5 × 10^{-3} mol) and (phenylethoxycarbene)pentacarbonylchromium (**6**) (1 g, 3 × 10^{-3} mol) in toluene (10 mL) was heated at 55–60 °C for 4 h with 150 mg of CuCl. The disappearance of the carbene complex was monitored by TLC. After evaporation, the crude reaction product was chromatographed on Florisil at -10 °C with pentane/CH_2Cl_2 (5/1). The diphosphetane complex **3** was thus obtained in 31.6% yield (1.2 g): ^{31}P NMR (toluene) δ -77.80 and -69.07 (^1J(P–P) = 97.7 Hz). The other characteristics of this product are given in ref 1.

Table I. Positional Parameters and Their Estimated Standard Deviations for the Heavy Atoms in $C_{22}H_{17}O_6PW$[a]

atom	*x*	*y*	*z*	*B*, Å^2
W	0.74289 (2)	0.40511 (1)	0.23210 (1)	3.158 (3)
P	0.8746 (1)	0.2253 (1)	0.1597 (1)	3.11 (2)
Cl	0.8236 (4)	0.0607 (4)	0.1616 (4)	3.71 (9)
C2	0.8113 (5)	-0.0110 (4)	0.0314 (5)	4.3 (1)
C3	0.8577 (4)	0.0951 (4)	-0.0179 (4)	3.76 (9)
C4	0.7722 (5)	0.1094 (5)	-0.1290 (4)	4.2 (1)
C5	0.8227 (6)	0.1886 (6)	-0.1891 (5)	5.9 (1)
C6	0.7475 (8)	0.2027 (7)	-0.2934 (6)	7.8 (2)
C7	0.6182 (8)	0.1357 (7)	-0.3376 (6)	7.4 (2)
C8	0.5657 (7)	0.0569 (7)	-0.2798 (6)	6.7 (2)
C9	0.6422 (5)	0.0429 (6)	-0.1746 (5)	5.2 (1)
O10	0.8108 (4)	0.0349 (3)	0.2672 (3)	4.94 (8)
C11	0.7906 (7)	-0.1073 (5)	0.2441 (6)	6.0 (1)
C12	0.818 (1)	-0.1129 (7)	0.3750 (7)	9.5 (2)
C13	1.0502 (4)	0.2730 (4)	0.2269 (4)	3.41 (8)
C14	1.1124 (5)	0.2094 (5)	0.2976 (4)	4.2 (1)
C15	1.2479 (5)	0.2506 (6)	0.3477 (5)	5.2 (1)
C16	1.3182 (5)	0.3514 (7)	0.3257 (6)	5.5 (1)
C17	1.2563 (5)	0.4134 (5)	0.2548 (5)	5.6 (1)
C18	1.1227 (5)	0.3762 (5)	0.2067 (5)	4.6 (1)
C19	0.5784 (5)	0.2810 (6)	0.1024 (6)	5.2 (1)
C20	0.6323 (5)	0.5434 (5)	0.2955 (5)	4.7 (1)
C21	0.9041 (5)	0.5382 (5)	0.3650 (5)	4.3 (1)
C22	0.6996 (5)	0.3358 (5)	0.3700 (5)	4.7 (1)
C23	0.7867 (7)	0.4754 (6)	0.0982 (5)	6.0 (1)
O19	0.4829 (4)	0.2172 (7)	0.0340 (6)	9.4 (2)
O20	0.5681 (4)	0.6224 (4)	0.3323 (5)	7.5 (1)
O21	0.9931 (4)	0.6135 (5)	0.4360 (5)	6.8 (1)
O22	0.6711 (5)	0.2954 (4)	0.4443 (4)	7.3 (1)
O23	0.8147 (7)	0.5232 (5)	0.0283 (5)	10.6 (2)

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

Reaction of the 7-Phosphanorbornadiene Complex 7 with (Phenylethoxycarbene)pentacarbonyltungsten. A solution of the 7-phosphanorbornadiene complex **7** (1.8 g, 3.5 × 10^{-3} mol) and (phenylethoxycarbene)pentacarbonyltungsten (**2**) (1 g, 2.2 × 10^{-3} mol) in toluene (40 mL) was heated at 55–60 °C for 1 night with 30 mg of CuCl. After chromatography as usual, a mixture of **5** and **8** was obtained and characterized as described in the Discussion (yield 400 mg, ca. 32% overall).

(1,2,2-Triphenylphosphaethylene)pentacarbonyltungsten (13). A solution of the 7-phosphanorbornadiene complex 1 (1.45 g, 2.2 × 10^{-3} mol) and (diphenylcarbene)pentacarbonyltungsten (**12**[4] (1 g, 2 × 10^{-3} mol) in toluene (20 mL) was heated at 60 °C for 15 min with 50 mg of CuCl. According to TLC, the carbene had completely disappeared. After chromatography with pentane on florisil at -20 °C, 500 mg of **13** was obtained as a yellow microcrystalline powder (41%): mp 105 °C dec; see the Discussion for the ^{13}C NMR, ^{31}P NMR, and mass spectra; IR (CH_2Cl_2) ν(CO) 2070 s, 1950 vs cm^{-1}. Anal. Calcd for $C_{24}H_{15}O_5PW$: C, 48.17; H, 2.50. Found: C, 47.89; H, 2.68. The product appears to be unstable upon standing.

(4-Ethoxy-1,2-diphenyl-1,2-dihydrophosphete)pentacarbonyltungsten (15a,b). A solution of the 7-phosphanorbornadiene complex 1 (1 g, 1.53 × 10^{-3} mol) and (ethoxystyrylcarbene)pentacarbonylchromium (**14**)[7] (0.4 g, 1.13 × 10^{-3} mol) in toluene (10 mL) was heated at 55 °C for 3 h with 50 mg of CuCl. After chromatography on silica gel with pentane/CH_2Cl_2 (4/1), 300 mg of **15** was obtained as a mixture of two isomers (44.8%). Slow recrystallization in CH_2Cl_2/pentane (2/1) allowed the separation of the two isomers. See the Discussion for the ^{13}C NMR, ^{31}P NMR, and mass spectra of the mixture. Major isomer: mp 99 °C; ^{1}H NMR ($CDCl_3$) δ 1.48 (t, ^3J(H–H) = 7.07 Hz, 3 H, CH_3), 3.83 (dd, ^2J(H–P) = 8.2 Hz, 1 H, PhC*H*), 4.18 (q, 2 H, OCH_2),

Table II. Positional Parameters for the Hydrogen Atoms in $C_{22}H_{17}O_6PW$[a]

atom	x	y	z	B, Å^2
H2	0.774 (6)	−0.115 (7)	−0.039 (6)	5.7*
H3	0.938 (6)	0.098 (6)	−0.031 (6)	4.9*
H5	0.909 (7)	0.246 (8)	−0.146 (7)	7.5*
H6	0.786 (9)	0.233 (9)	−0.357 (8)	10.0*
H7	0.572 (8)	0.155 (9)	−0.412 (8)	9.7*
H8	0.474 (8)	0.011 (8)	−0.294 (8)	8.7*
H9	0.610 (7)	−0.009 (7)	−0.122 (7)	6.8*
H14	1.060 (7)	0.132 (7)	0.316 (6)	5.6*
H15	1.298 (7)	0.209 (7)	0.406 (7)	6.9*
H16	0.415 (7)	0.363 (7)	0.359 (7)	7.0*
H17	1.298 (8)	0.515 (8)	0.247 (7)	7.1*
H18	1.078 (7)	0.421 (7)	0.167 (6)	5.8*
H111	0.689 (8)	−0.152 (8)	0.186 (7)	8.0*
H112	0.853 (8)	−0.145 (8)	0.202 (8)	8.0*
H121	0.82 (1)	−0.17 (1)	0.39 (1)	11.8*
H122	0.95 (1)	−0.07 (1)	0.390 (9)	11.8*
H123	0.81 (1)	−0.04 (1)	0.44 (1)	11.8*

[a] Parameters with an asterisk were refined isotropically.

5.35 (dd, ^3J(H–P) = 36.2 Hz, ^3J(H–H) = 1.2 Hz, 1 H, CH=), 7.26–7.70 (m, 10 H, Ph). Minor isomer: mp 92 °C. Anal. Calcd for $C_{22}H_{17}O_6PW$: C, 44.60; H, 2.87. Found: C, 44.80; H, 2.78.

4-Ethoxy-1,2-diphenyl-1,2-dihydrophosphete *P*-Oxide (16). A solution of complex **15** (0.3 g, 5×10^{-4} mol) in CH_2Cl_2 (5 mL) was treated at −30 °C with pyridinium tribromide (0.16 g, 5×10^{-4} mol). After 1 h of stirring, 2,2′-bipyridyl (0.16 g, 1×10^{-3} mol) was added. After additional stirring for 1.5 h at room temperature, the solvent was evaporated. The excess of 2,2′-bipyridyl was extracted from the residue with pentane. The residue was then dissolved in CH_2Cl_2 and chromatographed on silica gel with pentane/ethyl acetate (4/1). The oxide **16** (70 mg, 49%) was thus obtained: mp 70 °C; ^{1}H NMR ($CDCl_3$) δ 1.34 (t, ^3J(H–H) = 7.06 Hz, 3 H, CH_3), 4.08 (q, 2 H, OCH_2), 4.10 (dd, ^2J(H–P) = 12.5 Hz, 1 H, C*H*Ph), 5.96 (dd, ^3J(H–P) = 65.6 Hz, ^3J(H–H) = 1.9 Hz, 1 H, CH=), 7.26–7.94 (m, 10 H, Ph); ^{13}C NMR ($CDCl_3$) δ 14.74 (s, CH_3), 50.82 (d, ^1J(C–P) = 58.2 Hz, *C*HPh), 67.49 (d, ^3J(C–P) = 9 Hz, OCH_2), 113.57 (d, ^2J(C–P) = 8.1 Hz, *C*h=), 127.39–136.94 (Ph), 160.20 (d, ^1J(C–P) = 83.8 Hz, *C*OEt); ^{31}P NMR ($CDCl_3$) δ 22.95; mass spectrum, (EI, 70 eV), m/z (relative intensity) 284 (M, 15), 255 (M − Et, 100). Anal. Calcd for $C_{17}H_{17}O_2P$: C, 71.83; H, 5.98. Found: C, 71.13; H, 6.48.

X-ray Data Collection and Processing. Crystals of the title compound are triclinic, space group $P\bar{1}$, with cell parameters a = 10.519 (1) Å, b = 10.887 (1) Å, c = 11.134 (1) Å, α = 112.78 (2)°, β = 98.15 (2)°, γ = 97.13 (2)°, V = 1141.2 (7) Å^3, Z = 2, d = 1.723 g cm^{-3}, and μ = 52.705 cm^{-1}. A crystal fragment having dimensions of 0.30 × 0.26 × 0.22 mm was used to collect intensity data on a Enraf-Nonius CAD4 diffractometer. Data collection was conducted at room temperature in the $\theta/2\theta$ scan mode with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A total of 6622 reflections were measured in the range $1 < \theta < 30°$. A total of 5152 of these had $I > 3\sigma(I)$ and were used in all subsequent calculations.

The crystal structure was determined by using the Enraf-Nonius SDP structure determination package running on a Digital Equipment Micro-Vax II. Empirical absorption corrections were applied. All heavy atoms were refined by using anisotropic temperature factors. All hydrogen atoms positions were determined from a final difference Fourier map and were assigned a fixed isotropic thermal parameter equal to 1.3 times the equivalent B of the attached carbon atom. Their coordinates were refined in the final least-squares cycles. The least-squares refinement converged to R_F = 0.034, R_{wF} = 0.042, and goodness of fit = 1.097, with p = 0.06 in $\sigma^2(F^2) = \sigma^2_{\text{counts}} + (pI)^2$.

Registry No. **1**, 82265-64-3; **2**, 36834-98-7; **3**, 105762-35-4; (*Z*)-**5**, 105814-79-7; (*E*)-**5**, 105727-70-6; **6**, 26160-57-6; **7**, 82265-63-2; (*Z*)-**8**, 115140-71-1; (*E*)-**8**, 115223-67-1; **12**, 50276-12-5; **13**, 115140-72-2; **14**, 104267-43-8; **15** (isomer 1), 115140-73-3; **15** (isomer 2), 115223-68-2; **16** (isomer 1), 115093-19-1; **16** (isomer 2), 115093-20-4.

Supplementary Material Available: Tables III through V, positional and thermal displacement parameters, bond distances, and bond angles, respectively (5 pages); Table VI, a listing of computed and observed structure factor amplitudes (59 pages). Ordering information is given on any current masthead page.