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The Ene Reaction of Phosphaalkynes with Pentacarbonyltungsten Complexes of Phosphaalkenes[1]

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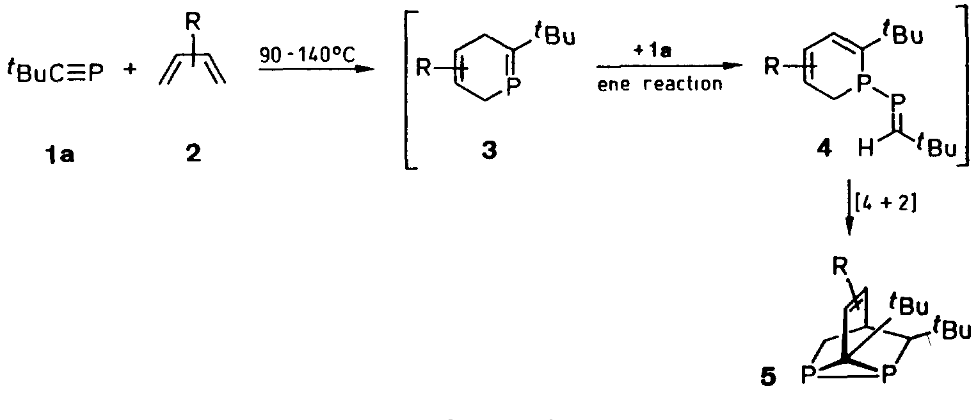
Abstract: The $W(CO)_5$-phosphaalkene complexes **9a**, **b**, and **11** take part in ene reactions with the phosphaalkynes **1a-c** to furnish the phosphinophosphaalkenes **10a-c** and **12a**, **b** containing the same metal fragment. In the reaction of **13** with **1a**, the ene product **14** undergoes partial isomerization to the diphosphirane complex **15**. Ene reactions of the *P*-silyl,*C*-silyloxy-substituted phosphaalkene complex **19** with **1a-c** follow the normal course to yield **20a-c**

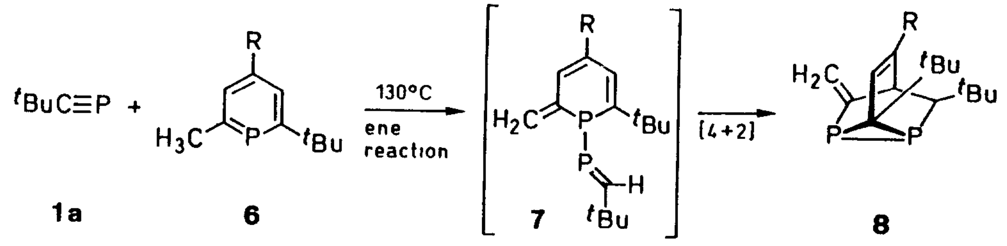
From the reactions of the phosphaalkyne **1a**[2] with 2,3-dimethyl-2-butene[3] and 1,2,3,4,5-pentamethylcyclopentadiene[4], it is known that ene reactions occur between the partners in which the P/C triple bond serves as the enophile and the olefin as the ene. The question of whether phosphaalkenes with hydrogen atoms in the ß position relative to the heteroatom can also behave as enes towards **1** has not been answered with certainty although there are some indications for such a reaction process.



Scheme 1

For example, the formation of the diphosphatricyclooctenes **5** has been observed in the reaction of **1a** with the 1,3-butadienes **2** in a molar ratio of 2:1. The formation of such a product can only be explained by the assumption that the initial Diels-Alder reaction to yield **3** is followed by an ene reaction of the latter with the second equivalent of the phosphaalkyne **1** to furnish **4**. This step is responsible for the P-P bond formation and represents the first stage in the construction of the diphosphirane unit which is concluded by an intramolecular [4 + 2] cycloaddition reaction to **5**[3] (Scheme 1).

An ene reaction has also be proposed to account for the formation of the polycyclic products **8** from the reactions of **1a** with the λ^3-phosphinines **6** (≡ "enophile") under thermal conditions. Again, the intermediate **7**, which cannot be isolated, is indispensible for a plausible explanation of the formation of **8**. The reaction step leading to the tricyclic system is once more an intramolecular Diels-Alder reaction[5] (Scheme 2).



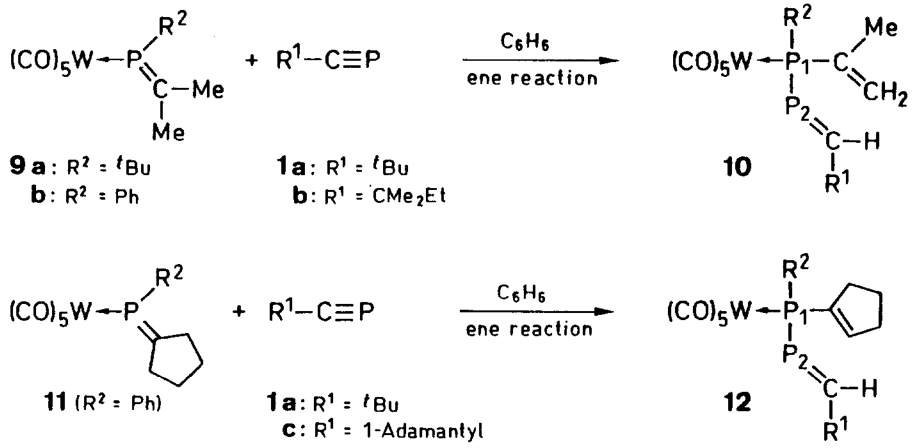
Scheme 2

With these results in mind, we have addressed the question of whether it is possible to isolate the ene products directly from reactions of phosphaalkynes **1** with phosphaalkenes. As enophiles we have chosen the pentacarbonyltungsten complexes of constitutionally suitable phosphaalkenes (**9**, **11**, **13**, **19**). Experience has shown that such compounds are more stable – albeit somewhat less reactive – and can be manipulated more easily.

RESULTS AND DISCUSSION

Ene Reactions of **1a-c** *with the* $W(CO)_5$ *Complexes* **9a, b,** *and* **11**

The phosphaalkene-pentacarbonyltungsten complexes **9a**, **b**, and **11** containing two allylic hydrogen atoms (which are thus sterically easily accessible on the ene system) react with the phosphaalkynes **1a-c** in benzene at temperatures between 25 and 45 °C to furnish the ene products **10a-c** and **12a**, **b** (Scheme 3). The reaction rate of the ene **11** is considerably higher than those of **9a** and **b**.



Compound	R^1	R^2	Temperature	Time
10a	^{t}Bu	^{t}Bu	25°C	3h
10b	^{t}Bu	Ph	35°C	3h
10c	CMe_2Et	Ph	45°C	5h
12a	^{t}Bu	Ph	25°C	0.5h
12b	1-Adamantyl	Ph	25°C	1h

Scheme 3

When the phosphaalkyne is employed in a 10% excess, the phosphaalkene complexes react quantitatively, as demonstrated by ^{31}P-NMR monitoring of the reactions. After removal of the solvent and excess enophile under reduced pressure, compounds **10a** and **b** were obtained in quantitative yields in the pure state. Purification by column chromatography was necessary in the cases of the ene products **10c** and **12a**, **b**, which resulted in lower yields (63-80%).

The molecular masses of **10a-c** (pale yellow oils) and **12a**, **b** (yellow solids) were determined by mass spectrometry; in the cases of crystalline solids, satisfactory elemental analyses were also obtained. All the proton signals in the ^{1}H-NMR spectra can be assigned. Evidence in favour of the postulated reaction process is provided by the appearance of signals for olefinic protons with characteristic ^2J(H,P) and ^3J(H,P) coupling constants that are not present in the starting materials (see Experimental Section).

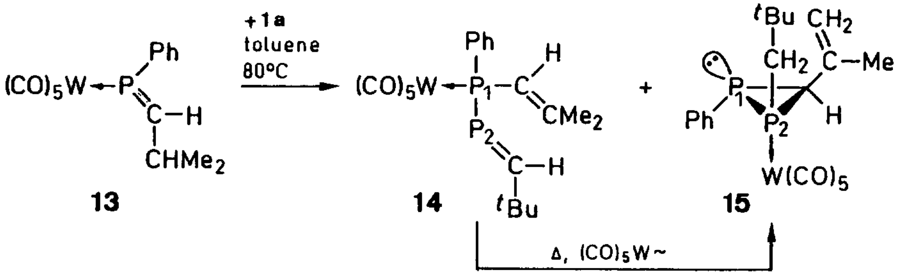
The ^{31}P-NMR signals (Table 1) also reflect the proposed course for the ene reaction; the original $\lambda^3\sigma^2$ phosphorus atoms in **9** and **11**[6] experience pronounced highfield shifts to appear at $\delta = -6.0$ to $+37.6$ with ^1J(P,W) coupling constants of 225-231 Hz, indicative of their phosphane character. The conversion of the $\lambda^3\sigma^1$-phosphorus atom of **1**[6] to the $\lambda^3\sigma^2$-phosphorus atoms of **10** and **12** can be recognized by the enormous lowfield shifts (δ = 227.7-236.2). At the same time, ^{13}C-NMR signals at δ = 211.16-216.54 with ^1J(C,P) coupling constants of 54.3-55.5 Hz are indicative of the formation of new phosphaalkene units.

Table 1. ^{31}P- and Selected ^{13}C-NMR Data of the Ene Products **10**, **12**, and **20** (C_6D_6).

Compound	δP_2	δP_1 [^1J(P,W)]	^1J(P1,P2)	δC=P [^1J(PC)]
10a	227.7	37.6 [225 Hz]	266 Hz	216.5 [54.3 Hz]
10b	229.0	14.8 [231 Hz]	256 Hz	212.1 [55.4 Hz]
10c	236.2	15.5 [231 Hz]	256 Hz	211.2 [55.5 Hz]
12a	229.6	−6.5 [226 Hz]	251 Hz	212.4 [55.4 Hz]
12b	230.6	−6.0 [226 Hz]	254 Hz	212.3 [55.2 Hz]
20a	226.8	−57.3 [209 Hz]	251 Hz	215.3 [56.1 Hz]
20b	231.4	−56.4 [212 Hz]	255 Hz	215.1 [56.9 Hz]
20c	228.1	−57.4 [209 Hz]	254 Hz	215.8 [55.6 Hz]

Diphosphirane (**15**) *Formation in the Ene Reaction* **13** + **1a**

If the phosphaalkene complex only possesses one allylic hydrogen atoms, as in the case of **13**, the rate of the ene reaction with **1a** is reduced significantly; long heating of the reactants in benzene at 80 °C is necessary to achieve quantitative reaction.



Scheme 4

A simple product palette is obtained when the reaction is interrupted after 24 h. ^{31}P-NMR spectroscopic analysis of the reaction mixture reveals the presence of a 1:3 mixture of the diphosphane complex **14** [δ = 238.9 (P2), −12.0 (P1), ^1J(P,P) = 249.8 Hz] and two stereoisomeric diphosphirane complexes [δ = −132.4 and −146.8, ^1J(P,P) = 168.0 Hz (≡ **A**) and δ = −121.4 and −147.1, ^1J(P,P) = 147.0 (≡ **B**). Column chromatography on silica gel with pentane and subsequent recrystallization from the same solvent results in the separation of the major isomer **A** which was identified as the diphosphirane-pentacarbonyltungsten complex **15**.

^{31}P-NMR spectroscopic monitoring of the reaction course reveals that the disphosphirane is formed from **14** by a thermal process and is accompanied by a shift of the $W(CO)_5$ fragment. The principle of such "transcomplexation reactions" at skeletal phosphorus atoms has been reported previously.[7] The isomerization of **14** to **15** may be interpreted as an intramolecular ene reaction in which the alkene unit functions as the ene and the phosphaalkene unit as the enophile. But also a homodienyl-1,5-hydrogen shift could be proposed to explain this isomerization.[8,9]

The NMR data of **15** are in accord with the proposed diphosphirane structure but do not allow any conclusions to be drawn concerning the stereochemistry. Above all, the highfield ^{31}P-NMR signals (see above)[10] are indicative of the formation of the three-membered ring. Final confirmation of the structure of **15** was provided by an X-ray crystallographic analysis which also demonstrated the spatial arrangements of the substituents on the ring. An ORTEP plot of the molecule is shown in Figure 1 and selected bonding and torsional angles are listed in Table 2.

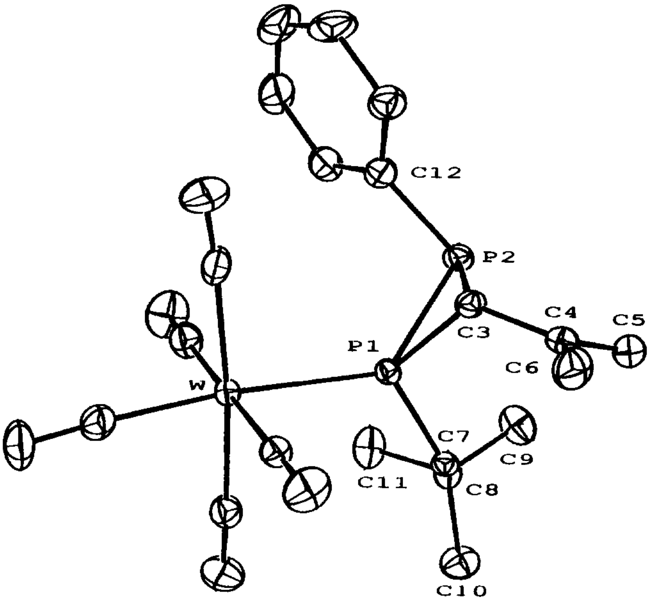


Fig. 1 ORTEP plot of the diphosphirane **15**.

When the bond lengths in the diphosphirane ring of **15** (Table 2) are compared with those of **5** [R = H; P-P 2.183(2), P-C 1.886(4) and 1.888(4) Å][3] they are found to be somewhat smaller. This is also true for the internal P-P-C angle in the diphosphirane **15** [54.2(2)° as compared to 54.7(1) and 54.6(1)°],[3] while the situation is reversed at carbon [P-C-P angle = 71.6(2)° compared with 70.7(2)°].[3]

Ene Reactions of **1a-c** *with the* $W(CO)_5$ *Complex* **19** *(R = Me)*

In order to verify whether other phosphaalkenes [or their $W(CO)_5$ complexes] with suitable constitutions can act as enophiles in ene reactions with the phosphaalkynes **1**, we have prepared compounds of the type **19**. These substrates offer the additional possibility of extending the synthetic scope of the reaction by a subsequent cleavage of hexamethyldisiloxane.

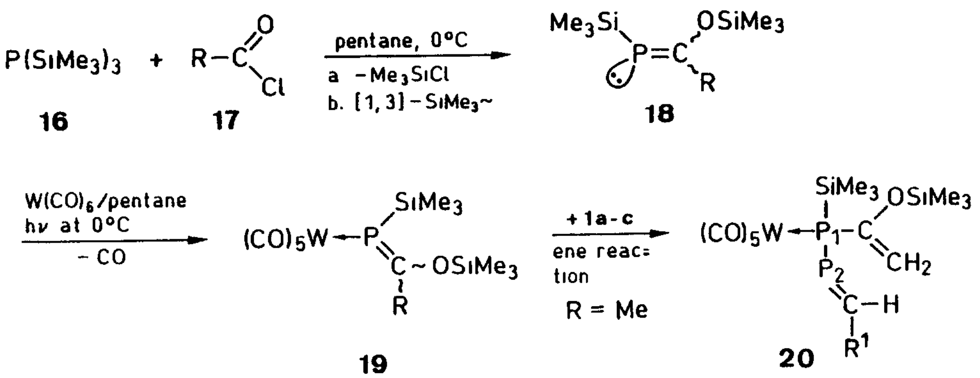
Table 2. Selected Bond Lengths, Bond Angles, and Torsional Angles in **15**.

		bond lengths [Å]			
W-P1	2.506(1)	P1-C7	1.838(6)	C3-C4	1.484(8)
P1-P2	2.178(2)	P2-C3	1.862(6)	C4-C5	1.319(9)
P1-C3	1.863(5)	P2-C12	1.820(6)	C4-C6	1.500(9)
		bond angles [°]			
W-P1-P2	131.2(7)	P2-P1-C7	107.2(2)	C3-P2-C12	104.0(3)
W-P1-C3	120.0(2)	C3-P1-C7	107.9(2)	P1-C3-P2	71.6(2)
W-P1-C7	118.6(2)	P1-P2-C3	54.2(2)	P1-C3-C4	123.0(4)
P2-P1-C3	54.2(2)	P1-P2-C12	103.1(2)	P2-C3-C4	120.4(4)
		torsional angles [°]			
W-P1-P2-C3	100.83(0.22)	W-P1-C3-P2	-121.34(0.13)	C7-P1-C3-C4	-16.12(0.51)
W-P1-P2-C2	2.92(0.23)	W-P1-C3-C4	123.84(0.40)	P1-P2-C3-C4	117.99(0.47)
C3-P1-P2-C12	-97.91(0.29)	P2-P1-C3-C4	-114.81(0.49)	C12-P2-C3-P1	96.24(0.23)
C7-P1-P2-C3	-99.92(0.27)	C7-P1-C3-P2	98.70(0.22)	C12-P2-C3-C4	-145.77(0.43)
C7-P1-P2-C12	162.16(0.26)				

Thus, for example, when tris(trimethylsilyl)phosphane (**16**) was allowed to react with acetyl chloride (**17**; R = Me) at 0 °C in pentane, the phosphaalkene **18** (R = Me) was formed in a reaction sequence comprising cleavage of chlorotrimethylsilane and subsequent, rapid [1,3]-shift of a trimethylsilyl group from phosphorus to oxygen.[11,12,13] Since compound **18** possesses only a relatively low kinetic stability, it was immediately photolyzed with hexacarbonyltungsten at the same temperature to furnish the complex **19** (R = Me; 78%) which is more convenient to handle. The usually employed ligand exchange reaction with $W(CO)_5 \cdot THF$ was not successful with **18**. Instead of **19**, complexes of the type $(CO)_5W \leftarrow PH_2\text{-CO-R}$ were obtained. Even when meticulously dried tetrahydrofuran was used as the solvent, both silyl groups were hydrolytically cleaved.[14] The *Z*/*E*-ratio of the two geometric isomers was approximately 5:1 (by NMR spectroscopy). The individual isomers were identified by ^{31}P-NMR spectroscopy whereby the *Z*-isomer is assigned the signal at lower field (δ = 81.1; *E*-isomer, δ = 70.5). This well-known phenomenon[13] in phosphaalkene chemistry remains unchanged in the case of "end-on" coordination of the $W(CO)_5$ fragment.[14]

The existence of geometric isomers of **19** has no significance for the subsequent reactions since the P/C double bond is saturated in the process.

Phosphaalkene complexes with sterically more demanding substituents (**19**; R = *i*Pr, CH_2-*t*Bu) can be prepared analogously,[14] but none of them reacted with **1a** in the sense of an ene reaction. Steric factors are thus apparently of major significance for the phospha-ene reaction.



Compound	R^1	Temperature	Time
20a	^{t}Bu	25°C	1h
20b	CMe_2Et	25°C	1h
20c	1-Adamantyl	25°C	1h

Scheme 5

However, when the phosphaalkene complex **19** (R = Me) is allowed to react with the phosphaalkynes **1a-c** in toluene at room temperature, the ene reaction takes place relatively rapidly and highly selectively through P/P bond formation to furnish the diphosphanes **20a-c** as deep red, oily products. In particular, a comparison of the ^{31}P- (see Table 1) and ^{13}C-NMR data of **20a-c** with those of **10a-c** and **12a, b** clearly indicate that all ene products contain a 2,3-diphospha-1,4-diene chain. Although the products **20a-c** were pure according to NMR spectroscopy, satisfactory elemental analyses could not be obtained; presumably as a consequence of the extreme sensitivity of the P/Si bond towards hydrolysis. The configurations of the ene products **10a-c**, **12a, b**, and **20a-c** could not be defined on the basis of the NMR data alone. However, with the help of general steric considerations, it is reasonable to assume that the phosphane substituent and the R^1 groups have a *trans*-orientation.

EXPERIMENTAL SECTION

Elemental analyses: Service d'analyse du CNRS, Gif-sur-Yvette, France and Analytiklabor des Fachbereichs Chemie der Universität Kaiserslautern (Perkin-Elmer Elemental Analyzer 240). – ^{1}H-NMR spectra: Bruker AC 200 SY and Varian EM 390 spectrometers (tetramethylsilane as internal standard). – ^{13}C-NMR spectra: Bruker AC 200 SY and Varian AM 400 spectrometers (tetramethylsilane as internal standard). – ^{31}P-NMR spectra: Bruker WP 200 and Bruker AM 400 spectrometers (85% H_3PO_4 as external standard). – Mass spectra: Shimadzu GC-MS QP 1000 and Finnigan MAT 90 spectrometers. – All reactions were carried out under argon (Schlenk tube technique); before use the reaction vessels were evacuated, heated, and flushed with argon. Anhydrous solvents were employed and were distilled and stored under argon prior to use.

The phosphaalkynes **1a**,[15] **1b**,[12] and **1c**[13] as well as the phosphaalkene-pentacarbonyltungsten complexes **9a,b**,[16] **11**,[17] and **13**[16] were prepared according to the reported procedures.

Preparation of Complexes **10a-c** *and* **12a,b**; *General Procedure*

A solution of the phosphaalkene complex **9a**, **b**, or **11** (0.2 mmol) in 2 ml benzene was allowed to react with a 10% excess of the phosphaalkyne **1a-c** (see Scheme 3 for reaction times and temperatures). The progress of the reaction was monitored by ^{31}P-NMR spectroscopy and the final products were either isolated directly after evaporation of the solvent and excess phosphaalkyne or worked-up by chromatography through a short column of silica gel with hexane as eluent ($R_F \approx 0.8$).

*1-*tert*-Butyl-2-(2,2-dimethylpropylidene)-1-(2-propenyl)diphosphane-1-pentacarbonyltungsten* (**10a**). Yield: 0.11 g (100%), pale yellow oil. - ^{1}H-NMR (C_6D_6): δ = 1.10 [d, ^{4}J(H,P) = 2.0 Hz, 9H, C-*t*Bu], 1.11 [d, ^{3}J(H,P) = 14.7 Hz, 9H, P-*t*Bu], 1.82 [d, ^{3}J(H,P) = 9.4 Hz, 3H, C-Me], 5.41 [d, ^{3}J(H,P) = 33.5 Hz, 1H, C=CH], 5.55 [d, ^{3}J(H,P) = 15.3 Hz, 1H, C=CH], 9.32 [dd, ^{2}J(H,P) = 22.5 Hz, ^{3}J(H,P) = 21.1 Hz, 1H, P=CH]. - ^{13}C-NMR (C_6D_6): δ = 25.8 [d, ^{2}J(C,P) = 10.1 Hz, P-C-$\underline{C}H_3$], 28.4 [pseudo-t, ^{2}J(C,P) = ^{3}J(C,P) = 5.0 Hz, P-C($\underline{C}H_3)_3$], 30.0 [d, ^{3}J(C,P) = 12.6 Hz, CH-C($\underline{C}H_3)_3$], 35.3 [dd, ^{1}J(C,P) = 15.6 Hz, ^{2}J(C,P) = 7.6 Hz, P-$\underline{C}(CH_3)_3$], 41.9 [pseudo-t, ^{2}J(C,P) = ^{3}J(C,P) = 13.6 Hz, CH-$\underline{C}(CH_3)_3$], 129.9 [pseudo-t, ^{2}J(C,P) = ^{3}J(C,P) = 6.5 Hz, =$\underline{C}H_2$], 141.1 [d, ^{1}J(C,P) = 12.1 Hz, P-$\underline{C}$-CH_3], 198.2 [d, ^{2}J(C,P) = 6.0 Hz, *cis*-$\underline{C}$O], 198.7 [d, ^{2}J(C,P) = 22.6, trans-$\underline{C}$O], 216.5 [d, ^{1}J(C,P) = 54.3 Hz, P=$\underline{C}$H]. - MS (70 eV): *m/z* (^{184}W) = 554 (M^+, 9%), 526 (M - CO, 28%), 498 (M - 2CO, 28%), 470 (M - 3CO, 40%), 385 (M - C_4H_9, - CO, 100%).

2-(2,2-Dimethylpropylidene)-1-phenyl-1-(2-propenyl)diphosphane-1-pentacarbonyltungsten (**10b**). Yield: 0.12 g (100%), pale yellow oil. - ^{1}H-NMR (C_6D_6): δ = 1.03 [d, ^{4}J(H,P) = 1.9 Hz, 9H, *t*Bu], 1.62 [d, ^{3}J(H,P) = 10.1 Hz, 3H, C-Me], 5.48 [d, ^{3}J(H,P) = 39.8 Hz, 1H, C=CH], 5.86 [d, ^{3}J(H,P) = 18.3 Hz, 1H, C=CH], 6.9-7.6 (m, 5H-aromatic), 9.04 [dd, ^{2}J(H,P) = 25.9 Hz, ^{3}J(H,P) = 20.9 Hz, 1H, P=CH]. - ^{13}C-NMR (C_6D_6): δ = 21.3 [d, ^{2}J(C,P) = 7.0 Hz, P-C-$\underline{C}H_3$], 30.0 [d, ^{3}J(C,P) = 12.1 Hz, C($\underline{C}H_3)_3$], 41.2 [pseudo-t, ^{2}J(C,P) = ^{3}J(C,P) = 12.8 Hz, $\underline{C}(CH_3)_3$], 129.2 [d, ^{3}J(C,P) = 9.1 Hz, phenyl-$\underline{C}$3/$\underline{C}$5], 129.6 [dd, ^{2}J(C,P) = 14.1 Hz, ^{3}J(C,P) = 6.5 Hz, =$\underline{C}H_2$], 130.1 [s, phenyl-$\underline{C}$4], 132.5 [dd, ^{2}J(C,P) = 9.6 Hz, ^{3}J(C,P) = 6.5 Hz, phenyl-$\underline{C}$2/$\underline{C}$6], 134.9 [dd, ^{1}J(C,P) = 32.2 Hz, ^{2}J(C,P) = 6.0 Hz, phenyl-$\underline{C}$1], 141.5 [d, ^{1}J(C,P) = 22.1 Hz, P-$\underline{C}$-CH_3], 197.4 [d, ^{2}J(C,P) = 6.0 Hz, *cis*-$\underline{C}$O], 199.6 [d, ^{2}J(C,P) = 22.6 Hz, *trans*-$\underline{C}$O], 212.1 [d, ^{1}J(C,P) = 55.4 Hz, P=$\underline{C}$H]. - MS (70 eV): *m/z* (^{184}W) = 574 (M^+, 38%), 546 (M - CO, 55%), 518 (M - 2CO, 21%), 490 (M - 3CO, 38%), 462 (M - 4CO, 100%).

2-(2,2-Dimethylbutylidene)-1-phenyl-1-(2-propenyl)diphosphane-1-pentacarbonyltungsten (**10c**). Yield: 0.09 g (80%), pale yellow oil. - ^{1}H-NMR (C_6D_6): δ = 0.67 [t, ^{3}J(H,H) = 7.4 Hz, 3H, ethyl-CH_3], 1.02 (s, 6H, CMe_2), 1.26 [q, ^{3}J(H,H) = 7.4 Hz, 2H, ethyl-CH_2], 1.62 [d, ^{3}J(H,P) = 10.2 Hz, 3H, C-Me], 5.46 [d, ^{3}J(H,P) = 39.5 Hz, 1H, C=CH], 5.88 [d, ^{3}J(H,P) = 18.3 Hz, 1H, C=CH], 6.9-7.6 (m, 5H-aromatic), 8.98 [dd, ^{2}J(H,P) = 26.1 Hz, ^{3}J(H,P) = 20.9 Hz, 1H, P=CH]. - ^{13}C-NMR (C_6D_6): δ = 9.0 (s, $CH_2\underline{C}H_3$), 21.3 [d, ^{2}J(C,P) = 8.1 Hz, P-C-$\underline{C}H_3$], 27.4 [d, ^{3}J(C,P) = 13.6 Hz, C($\underline{C}H_3)_2$], 36.0 [d, ^{3}J(C,P) = 8.6 Hz, $\underline{C}H_2CH_3$], 44.3 [pseudo-t, ^{2}J(C,P) = ^{3}J(C,P) = 11.6 Hz, $\underline{C}(CH_3)_2CH_2CH_3$], 129.2 [d, ^{3}J(C,P) = 9.3 Hz, phenyl-$\underline{C}$3/$\underline{C}$5], 129.6 [d, ^{2}J(C,P) = 6.9 Hz, =$\underline{C}H_2$], 130.1 (s, phenyl-$\underline{C}$4), 132.6 [dd, ^{2}J(C,P) = 9.2 Hz, ^{3}J(C,P) = 5.5 Hz, phenyl-$\underline{C}$2/$\underline{C}$6], 134.9 [dd, ^{1}J(C,P) = 32.0 Hz, ^{2}J(C,P) = 4.6 Hz, phenyl-$\underline{C}$1], 141.6 [d, ^{1}J(C,P) = 22 6 Hz, P-$\underline{C}$-CH_3], 197.4 [d, ^{2}J(C,P) = 6.1 Hz, *cis*-$\underline{C}$O], 199.6 [d, ^{2}J(C,P) = 22.5 Hz, *trans*-$\underline{C}$O], 211.2 [d, ^{1}J(C,P) = 55.5 Hz, P=$\underline{C}$H]. - MS (70 eV): *m/z* (^{184}W) = 588 (M^+, 26%), 560 (M - CO, 51%), 532 (M - 2CO, 15%), 504 (M - 3CO, 38%), 476 (M - 4CO, 87%), 448 (M - 5CO, 100%).

1-(1-Cyclopentenyl)-2-(2,2-dimethylpropylidene)-1-phenyldiphosphane-2-pentacarbonyltungsten (**12a**). Yield: 0.08 g (63%), yellow solid, m.p. 57 °C. - ^{1}H-NMR (C_6D_6): δ = 1.05 [d, ^{4}J(H,P) = 1.9 Hz, 9H, *t*Bu], 1.5-1.7 [m, 2H, cyclopentene-H4], 2.1-2.3 [m, 4H, cyclopentene-H3/H5], 6.53 [broad d, ^{3}J(H,P) = 9.7 Hz, 1H, cyclopentene-H2], 6.9-7.6 (m, 5H–aromatic), 9.13 [dd, ^{2}J(H,P) = 26.7 Hz, ^{3}J(H,P) = 21.0 Hz, P=CH]. – ^{13}C-NMR (C_6D_6): δ = 24.9 [d, ^{3}J(C,P) = 5.8 Hz, cyclopentene-$\underline{C}$4], 30.1 [d, ^{3}J(C,P) = 12.1 Hz, C($\underline{C}H_3)_3$], 34.4 [d, ^{2}J(C,P) = 13.0 Hz, cyclopentene-$\underline{C}$5], 35.0 [d, ^{3}J(C,P) = 4.7 Hz, cyclopentene-$\underline{C}$3], 41.1 [pseudo-t, ^{2}J(C,P) = ^{3}J(C,P) = 13.1 Hz, $\underline{C}(CH_3)_3$], 129.9 [d, ^{3}J(C,P) = 9.1 Hz, phenyl-$\underline{C}$3/$\underline{C}$5], 130.0 [s, phenyl-$\underline{C}$4], 132.1 [dd, ^{2}J(C,P) = 9.6 Hz, ^{3}J(C,P) = 6.0 Hz, phenyl-$\underline{C}$2/$\underline{C}$6], 135.3 [dd, ^{1}J(C,P) = 33.7 Hz, ^{2}J(C,P) = 6.0 Hz, phenyl-$\underline{C}$1], 138.7 [d, ^{1}J(C,P) = 31.2 Hz, cyclopentene-$\underline{C}$1], 146.9 [dd, ^{2}J(C,P) = 13.3 Hz, ^{3}J(C,P) = 4.3 Hz, cyclopentene-$\underline{C}$2], 197.6 [d, ^{2}J(C,P) = 6.5 Hz, *cis*-$\underline{C}$O], 199.8 [d, ^{2}J(C,P) = 21.1 Hz, *trans*-$\underline{C}$O], 212.5 [d, ^{1}J(C,P) = 55.4 Hz, P=$\underline{C}$H]. – MS (70 eV): *m/z* (^{184}W) = 600 (M^+, 21%), 572 (M – CO, 45%), 544 (M – 2CO, 15%), 516 (M – 3CO, 28%), 499 (M – P=CH-C_4H_9, 19%), 488 (M – 4CO, 81%), 460 (M – 5CO, 64%), 443 (M – 2CO, – P=CH-C_4H_9, 64%), 356 [$(CO)_5$WPH, 100%]. - Anal. calcd. for $C_{21}H_{22}O_5P_2W$ (600.16): C, 42.02; H 3.70. Found: C, 41.85; H, 3.46.

2-(1-Adamantylmethylene)-1-(1-cyclopentyl)-1-phenyldiphosphane-1-pentacarbonyltungsten (**12b**). Yield: 0.10 g (74%), yellow solid, m.p. 126 °C. - ^{1}H-NMR (C_6D_6): δ = 1.4-1.7 (m, 14H), 1.8 (broad s, 3H) and 2.2 (broad s, 4H) (adamantane and cyclopentene H), 6.57 [broad d, ^{3}J(H,P) = 9.8 Hz, 1H, cyclopentene H2], 6.9-7.6 (m, 5H–aromatic), 9.05 [dd, ^{2}J(H,P) = 27.0 Hz, ^{3}J(H,P) = 20.8 Hz, 1H, P=CH]. – ^{13}C-NMR (C_6D_6): δ = 24.9 [d, ^{3}J(C,P) = 6.0 Hz, cyclopentene-$\underline{C}$4], 28.6 [s, adamantane-$\underline{C}$3/$\underline{C}$5/$\underline{C}$7], 34.4 [d, ^{2}J(C,P) = 13.1 Hz, cyclopentene-$\underline{C}$5], 35.1 [d, ^{3}J(C,P) = 5.5 Hz, cyclopentene-$\underline{C}$3], 36.5 [s, adamantane-$\underline{C}$4/$\underline{C}$6/$\underline{C}$10], 43.0 [d, ^{3}J(C,P) = 12.1 Hz, adamantane-$\underline{C}$2/$\underline{C}$8/$\underline{C}$9], 43.8 [pseudo-t, ^{2}J(C,P) = ^{3}J(C,P) = 12. 6 Hz, adamantane-$\underline{C}$1], 129.9 [d, ^{3}J(C,P) = 9.1 Hz, phenyl-$\underline{C}$3/$\underline{C}$5], 130.0 (s, phenyl-$\underline{C}$4), 132.2 [dd, ^{2}J(C,P) = 10.1 Hz, ^{3}J(C,P) = 6.0 Hz, phenyl-$\underline{C}$2/$\underline{C}$6], 135.5 [dd, ^{1}J(C,P) = 35.1 Hz, ^{2}J(C,P) = 7.6 Hz, phenyl-$\underline{C}$1], 138.9 [d, ^{1}J(C,P) = 30.7 Hz, cyclopentene-$\underline{C}$1], 145.8 (dd, ^{2}J(C,P) = 13.6 Hz, ^{3}J(C,P) = 4.0 Hz, cyclopentene-$\underline{C}$2], 197.7 [d, ^{2}J(C,P) = 6.4 Hz, *cis*-$\underline{C}$O], 199.9 [d, ^{2}J(C,P) = 21.9 Hz, *trans*-$\underline{C}$O], 212.3 [d, ^{1}J(C,P) = 55.2 Hz, P=$\underline{C}$H]. – MS (70 eV): *m/z* (^{184}W) = 676 (M – 2H, 9%), 649 (M – 1H, – CO, 36%), 594 (M – 3CO, 36%), 566 (M – 4CO, 68%), 538 (M – 5CO, 77%), 536 (M – 2H, – 5CO, 100%). – Anal. calcd. for $C_{27}H_{28}O_5P_2W$ (678.27): C, 47.81; H, 4.16. Found: C, 47.92; H, 4.03.

2-(2,2-Dimethylpropyl)-1-phenyl-3-(2-propenyl)diphosphirane-2-pentacarbonyltungsten (**15**).

The phosphaalkene complex **13** (0.95 g, 1.9 mmol) was heated with an excess of the phosphaalkyne **1a** (0.40 g, 4.0 mmol) in toluene (3 ml) at 80 °C for 24 h during which time the metal complex reacted completely (^{31}P-NMR monitoring). The resultant mixture contained excess **1a**, some diphosphane **14** {^{31}P-NMR: δ = –12.0 [d, ^{1}J(P,P) = 249.8 Hz, P1)], 238.9 [d, ^{1}J(P,P) = 249.8 Hz, P2]}, and the two stereoisomers of the diphosphirane in comparable amounts. After evaporation under reduced pressure and two passages through a column (2.5 x 9 cm) of silica gel (26 g) with *n*-pentane (200 ml) as eluent under ^{31}P-NMR control of the purification steps, pure **15** was obtained after crystallization from pentene at -20 °C as pale yellow crystals. Yield: 0.3 g (26%), m.p. 101 °C. – ^{1}H-NMR (C_6D_6): δ = 1.12 [d, ^{4}J(H,P) = 1.2 Hz, 9H, *t*Bu], 1.5-1.7 (m, 2H, P-CH_2), 1.79 (s, 3H, =C-Me), 2.72 [d, ^{2}J(H,P) = 5.2 Hz, 1H, cyclopropane H], 4.90 (s, 1H, =CH_2), 5.01 (s, 1H, =CH_2), 6.9-7.2 (m, 5H–aromatic). – ^{13}C-NMR (C_6D_6): δ = 25.2 [s, C($\underline{C}H_3$)=CH_2], 31.7 [pseudo-t, ^{3}J(C,P) = ^{4}J(C,P) = 6.1 Hz, C($\underline{C}H_3)_3$], 32.1 [d, ^{1}J(C,P) = 26.9 Hz, P-$\underline{C}H_2$], 39.9 [dd, ^{2}J(C,P) = 11.9 Hz, ^{3}J(C,P) = 4.7 Hz, $\underline{C}(CH_3)_3$], 41.7 [dd, ^{1}J(C,P) = 41.8 and 17.6 Hz, respectively, diphosphirane C], 115.9 [dd, ^{3}J(C,P) = 18.6 and 6.3 Hz, respectively, C(CH_3)=$\underline{C}H_2$], 129.5 [d, ^{4}J(C,P) = 3.0 Hz, phenyl-$\underline{C}$3], 129.8 (s, phenyl-$\underline{C}$4), 133.3 [dd, ^{2}J(C,P) = 15.2 Hz, ^{3}J(C,P) = 4.6 Hz, phenyl-$\underline{C}$2], 134.7 [d, ^{1}J(C,P) = 38.2 Hz, phenyl-$\underline{C}$1], 139.4 [dd, ^{2}J(C,P) = 12.3 and 7.6 Hz, respectively, $\underline{C}$(CH_3)=CH_2], 196.4 [d, ^{2}J(C,P)

= 7.5 Hz, *cis*-$\underline{C}$O], 197.7 [d, ^2J(C,P) = 31.0 Hz, *trans*-$\underline{C}$O]. - MS (70 eV): *m/z* (^{184}W) = 588 (M$^+$, 6%), 560 (M - CO, 47%), 504 (M - 3CO, 100%), 476 (M - 4CO, 40%), 448 (M - 5CO, 85%). - Anal. calcd. for $C_{20}H_{22}O_5P_2W$ (588.14): C, 40.84; H, 3.77. Found: C, 41.64; H, 3.91.

X-Ray Crystal Structure Analysis of **15**[18].

Crystals of **15** ($C_{20}H_{22}O_5P_2W$) were grown at -18 °C from a hexane solution of the compound. Data were collected at -150 ± 0.51 °C on an Enraf Nonius CAD4 diffractometer. The crystal structure was solved and refined using the MolEN package supplied by Enraf Nonius. The enantiomers of **15** crystallized separately in space group $P2_12_12_1$, a = 10.057(1) Å, b = 10.348(1) Å, c = 21.459(2) Å; V = 2233.28(64) Å^3; Z = 4; $D_{calc.}$ = 1.749 g/cm^{-3}; Mo K_α radiation (λ = 0.71073 Å), graphite monochromator; μ = 54.5 cm^{-1}; F(000) = 1144. A total of 3678 unique reflections were recorded in the range 2° ≤ 2θ ≤ 60.0°, of which 383 were considered as unobserved [$F^2 < 3.0\sigma(F^2)$], leaving 3295 for solution and refinement. A Patterson map yielded a solution for the tungsten and one of the two phosphorus atoms. The hydrogen atoms were included as fixed contributions in the final stages of the least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.08. The final agreement factors were R = 0.022, R_ω = 0.044, G.O.F = 0.99. These values were, respectively, R = 0.046, R_ω = 0.076, G.O.F = 1.66 for the enantiomeric structure.

(E/Z)-1-Trimethylsiloxyethylidene(trimethylsilyl)phosphane-pentacarbonyltungsten (**19**).

In an irradiation appartus at 0 °C under an argon atmosphere, a solution of tris(trimethylsilyl)phosphane (**16**; 3.1 ml, 10.7 mmol)[19] in pentane (20 ml) was added dropwise with stirring to a solution of acetyl chloride (**17**, R = Me; 0.77 ml, 10.7 mmol) in pentane (20 ml). The mixture was stirred at the same temperature for 1 h and hexacarbonyltungsten (4.0 g, 11.4 mmol) diluted in pentane (150 ml) was added. The mixture was irradiated (Philips HPK 125 W mercury high-pressure lamp) after renewed cooling to 0 °C for about 1.5 h. The reaction mixture was then evaporated under reduced pressure until excess hexacarbonyltungsten precipitated out. The supernatant solution was pipetted off and cooled to -20 °C whereupon the phosphaalkene complex **19** (mixture of *E/Z* isomers) separated as orange crystals. Yield: 4.50 g (78%), m.p. 116 °C. - ^{1}H-NMR (C_6D_6): Z-isomer, δ = 0.40 (s, 9H, OSiMe$_3$), 0.65 [d, ^3J(H,P) = 6.0 Hz, 9H, SiMe$_3$], 2.35 [d, ^3J(H,P) = 20.5 Hz, 3H, =C(Me)]; E-isomer, δ = 0.55 (s, 9H, OSiMe$_3$), 0.60 [d, ^3J(H,P) = 6.0 Hz, 9H, SiMe$_3$], 2.20 [d, ^3J(H,P) = 16.5 Hz, 3H, =C(Me)]. - ^{13}C-NMR (C_6D_6): Z-isomer, δ = 0.2 [s, OSi($\underline{C}H_3)_3$], 1.3 [d, ^2J(C,P) = 10.1 Hz, Si($\underline{C}H_3)_3$], 28.1 [d, ^2J(C,P) = 21.0 Hz, =C-$\underline{C}H_3$], 196.2 [d, ^2J(C,P) = 8.0 Hz, *cis*-$\underline{C}$O], 200.6 [d, ^2J(C,P) = 22.6 Hz, *trans*-$\underline{C}$O], 209.7 [d, ^1J(C,P) = 19.4 Hz, P=$\underline{C}$]; E-isomer, δ = 0.3 [s, OSi($\underline{C}H_3)_3$], 1.4 [d, ^2J(C,P) = 9.8 Hz, Si($\underline{C}H_3)_3$], 29.5 [d, ^2J(C,P) = 18.2 Hz, =C-$\underline{C}H_3$], 196.4 [d, ^2J(C,P) = 8.0 Hz, *cis*-$\underline{C}$O], 200.8 [d, ^2J(C,P) = 20.2 Hz, *trans*-$\underline{C}$O], 210.1 [d, ^1J(C,P) = 16.2 Hz, P=$\underline{C}$]. - ^{31}P-NMR (C_6D_6): E-isomer, δ = 70.5 [d, ^1J(P,W) = 206.0 Hz]; Z-isomer, δ = 81.1 [d, ^1J(P,W) = 198.0 Hz). - Anal. calcd. for $C_{13}H_{21}O_6PSi_2W$ (544.25): C, 28.69; H, 3.89. Found: C, 28.30; H, 3.60.

Preparation of Complexes **20a-c**; *General Procedure.*

To a solution of the phosphaalkene-pentacarbonyltungsten complex **19** (0.54 g, 1.0 mmol) in toluene (5 ml) was added with stirring at 25 °C the phosphaalkyne **1a**, **b**, or **c** (1.1 mmol). After 1 h, excess phosphaalkyne and the solvent were evaporated at 10^{-3} mbar (in the case of the reaction of **19** with **1c**, this is achieved by sublimation at 50 °C/10^{-3} mbar) to leave the pure (by NMR spectroscopy) products **20a-c** as deep-red oils in quantitative yield.

2-(2,2-Dimethylpropylidene)-1-trimethylsilyl-1-(1-trimethylsiloxyvinyl)-diphosphane-1-pentacarbonyltungsten (**20a**). ^{1}H-NMR (C_6D_6): δ = 0.20 (s, 9H, OSiMe$_3$), 0.41 [d, ^3J(H,P) = 6.0 Hz, 9H, SiMe$_3$], 1.20 [d, ^4J(H,P) = 2.5 Hz, 9H, =C-*t*Bu], 4.55 [d, ^2J(H,P) = 26.1 Hz, 1H, =CH$_2$], 4.80 [d, ^2J(H,P) = 14.2 Hz, 1H, =CH$_2$], 9.40 [dd, ^2J(H,P) = 27.0 Hz, ^3J(H,P) = 21.1 Hz, 1H, P=CH]. - ^{13}C-NMR (C$_6$D$_6$): δ = 0.1 [d, ^2J(C,P) = 7.6 Hz, Si($\underline{\mathrm{C}}$H$_3$)$_3$], 0.4 [s, OSi($\underline{\mathrm{C}}$H$_3$)$_3$], 30.4 [d, ^3J(C,P) = 12.1 Hz, C($\underline{\mathrm{C}}$H$_3$)$_3$], 42.1 [d, ^2J(C,P) = 12.1 Hz, $\underline{\mathrm{C}}$(CH$_3$)$_3$], 101.2 [d, ^2J(C,P) = 11.5 Hz, P-C=$\underline{\mathrm{C}}$H$_2$], 153.2 [dd, ^1J(H,P) = 30.2 Hz, ^2J(C,P) = 9.2 Hz, P-$\underline{\mathrm{C}}$=CH$_2$], 197.9 [d, ^2J(C,P) = 5.7 Hz, *cis*-$\underline{\mathrm{C}}$O], 199.3 [d, ^2J(C,P) = 20.8 Hz, *trans*-$\underline{\mathrm{C}}$O], 215.3 [d, ^1J(C,P) = 56.1 Hz, P=$\underline{\mathrm{C}}$]. - MS (70 eV): *m/z* (^{184}W) = 644 (M$^+$, 6%), 616 (M - CO, 9%), 504 (M - 5CO, 22%), 487 (M - 2CO, - P=CH-C$_4$H$_9$, 18%), 430 (M - 4CO, - P=CH-C$_4$H$_9$, 24%), 402 (M - 5CO, - P=CH-C$_4$H$_9$, 13%), 147 {P-C[OSi(CH$_3$)$_3$]=CH$_2$, 27%}, 73 [Si(CH$_3$)$_3$, 100%].

2-(2,2-Dimethylbutylidene)-1-trimethylsilyl-1-(1-trimethylsiloxyvinyl)-diphosphane-1-pentacarbonyltungsten (**20b**). ^{1}H-NMR (C$_6$D$_6$): δ = 0.15 (s, 9H, OSiMe$_3$), 0.24 [d, ^3J(H,P) = 6.0 Hz, 9H, SiMe$_3$], 0.80 [t, ^3J(H,H) = 7.1 Hz, 3H, ethyl-CH$_3$], 1.10 [d, ^4J(H,P) = 2.0 Hz, 6H, CMe$_2$], 1.30 [q, ^3J(H,H) = 7.1 Hz, ethyl-CH$_2$], 4.60 [d, ^3J(H,P) = 22.2 Hz, 1H, =CH$_2$], 4.80 [d, ^3J(H,P) = 8.4 Hz, 1H, =CH$_2$], 9.40 [dd, ^2J(H,P) = 27.0 Hz, ^3J(H,P) = 21.0 Hz, 1H, P=CH]. - ^{13}C-NMR (C$_6$D$_6$): δ = -0.1 [d, ^2J(C,P) = 7.6 Hz, Si($\underline{\mathrm{C}}$H$_3$)$_3$], 0.4 [s, OSi($\underline{\mathrm{C}}$H$_3$)$_3$], 9.1 (s, CH$_2\underline{\mathrm{C}}$H$_3$), 27.6 [d, ^3J(C,P) = 17.4 Hz, C($\underline{\mathrm{C}}$H$_3$)$_2$CH$_2$-CH$_3$] 35.8 [d, ^3J(C,P) = 8.5 Hz, $\underline{\mathrm{C}}$H$_2$CH$_3$], 45.1 [pseudo-t, ^2J(C,P) = ^3J(C,P) = 11.8 Hz, $\underline{\mathrm{C}}$(CH$_3$)$_2$CH$_2$-CH$_3$], 101.0 [d, ^2J(C,P) = 12.1 Hz, P-C=$\underline{\mathrm{C}}$H$_2$], 156.4 [dd, ^1J(H,P) = 36.7 Hz, ^2J(C,P) = 8.9 Hz, P-$\underline{\mathrm{C}}$=-CH$_2$], 197.8 [d, ^2J(C,P) = 5.7 Hz, *cis*-$\underline{\mathrm{C}}$O], 199.3 [d, ^2J(C,P) = 20.2 Hz, *trans*-$\underline{\mathrm{C}}$O], 215.1 [d, ^1J(C,P) = 56.9 Hz, P=$\underline{\mathrm{C}}$H]. - MS (70 eV): *m/z* (^{184}W) = 658 (M$^+$, 2%), 430 [M - 4CO, - P=CH-C(CH$_3$)$_2$-C$_2$H$_5$, 10%], 402 [M - 5CO, - P=CH-C(CH$_3$)$_2$C$_2$H$_5$, 12%], 147 {P-C[OSi(CH$_3$)$_3$]=CH$_2$, 100%}.

2-(1-Adamantylmethylene)-1-trimethylsilyl-1-(trimethylsiloxyvinyl)-diphosphane-1-pentacarbonyltungsten (**20c**). ^{1}H-NMR (C$_6$D$_6$): δ = 0.30 (s, 9H, OSiMe$_3$), 0.50 [d, ^3J(H,P) = 6.0 Hz, 9H, SiMe$_3$], 1.7-2.0 (m, 15H, adamantane), 4.90 [d, ^3J(H,P) = 20.5 Hz, 1H, =CH$_2$], 5.10 [d, ^3J(H,P) = 10.6 Hz, 1H, =CH$_2$], 9.50 [dd, ^2J(H,P) = 28.0 Hz, ^3J(H,P) = 22.1 Hz, 1H, P=CH]. - ^{13}C-NMR (C$_6$D$_6$): δ = 0.0 [d, ^2J(C,P) = 8.0 Hz, Si($\underline{\mathrm{C}}$H$_3$)$_3$], 0.5 [s, OSi($\underline{\mathrm{C}}$H$_3$)$_3$], 28.2 (s, adamantane-$\underline{\mathrm{C}}$3/$\underline{\mathrm{C}}$5/$\underline{\mathrm{C}}$7), 36.3 (s, adamantane-$\underline{\mathrm{C}}$4/$\underline{\mathrm{C}}$6/$\underline{\mathrm{C}}$10), 43.3 [d, ^3J(C,P) = 13.3 Hz, adamantane-$\underline{\mathrm{C}}$2/$\underline{\mathrm{C}}$8/$\underline{\mathrm{C}}$9], 44.6 [pseudo-t, ^2J(C,P) = ^3J(C,P) = 7.3 Hz, adamantane-$\underline{\mathrm{C}}$1], 100.9 [d, ^2J(C,P) = 10.4 Hz, P-C=$\underline{\mathrm{C}}$H$_2$], 156.5 [dd, ^1J(C,P) = 27.5 Hz, ^2J(C,P) = 10 1 Hz, P-$\underline{\mathrm{C}}$=CH$_2$], 197.8 [d, ^2J(C,P) = 5.7 Hz, *cis*-$\underline{\mathrm{C}}$O], 199.2 [d, ^2J(C,P) = 21.5 Hz, *trans*-$\underline{\mathrm{C}}$O], 215.8 [d, ^1J(C,P) = 55.6 Hz, P=$\underline{\mathrm{C}}$H]. - MS (70 eV): *m/z* (^{184}W) = 722 (M$^+$, 5%), 694 (M - CO, 8%), 582 (M - 5CO, 21%), 543 (M - P=CH-Ad, 13%), 404 (M - 5CO, - P=CH-Ad, 15%),147 {P-C[OSi(CH$_3$)$_3$]=CH$_2$, 100%}.

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REFERENCES AND NOTES

1. This work is considered as Part 66 of the series on Organophosphorus Compounds started by M. Regitz; for Part 65, see: Breit, B.; Regitz, M. *Synthesis* **1993**, in press.
2. For reviews on the reactivity of phosphaalkynes, see: Regitz, M.; Binger, P. *Angew. Chem.* **1988**, *100*, 1541-1565; *Angew. Chem., Int. Ed. Engl.* **1988**, *27,* 1484-1508. Regitz, M. *Chem. Rev.* **1990**, *90*, 191-213. Regitz, M. In: *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M.; Scherer, O.J. Eds; Thieme: Stuttgart, 1990, p. 58 *et seq.*

3. Fuchs, E. P. O.; Rösch, W.; Regitz, M. *Angew. Chem.* **1987**, *99*, 1058-1059; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1011-1012.
4. Annen, U.; Regitz, M. *Tetrahedron Lett.* **1988**, *29*, 1681-1684.
5. Annen, U. *Thesis*, University of Kaiserslautern 1989. See also: Regitz, M. In: *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M.; Scherer, O.J. Eds; Thieme: Stuttgart, 1990, p. 83 *et seq.*
6. For ^{31}P-NMR spectroscopic data of low-coordinated phosphorus compounds, see: Karaghiosoff, K. In: *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M.; Scherer, O.J. Eds; Thieme: Stuttgart, 1990, p. 463 *et seq.*
7. Mercier, F.; Ricard, L.; Mathey, F.; Regitz, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1305-1307.
8. Hoffmann, H. M. R.; *Angew. Chem.* **1969**, *81*, 597-618; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556-577.
9. Frey, H. M.; Walsch, R. *Chem. Rev.* **1969**, *69*, 103-124.
10. In the diphosphatricyclooctenes **5**, the phosphorus atoms experience an even higher shielding [$\delta = -165.5$ to -210.3, $^1J(\mathrm{P,P}) = 150.0$ to 158.7 Hz], presumably as a consequence of the incorporation of the diphosphirane unit in a polycyclic skeleton; for further information, see Ref.[3]
11. Becker, G. *Z. Anorg. Allg. Chem.* **1977**, *430*, 66-76.
12. Allspach, T.; Regitz, M.; Becker, G.; Becker, W. *Synthesis* **1986**, 31-36.
13. Rösch, W.; Vogelbacher, U.; Allspach, T.; Regitz, M. *J. Organomet. Chem.* **1986**, *306*, 39-53.
14. Slany, M. *Diploma Thesis*, University of Kaiserslautern 1991.
15. Rösch, W.; Hees, U.; Regitz, M. *Chem. Ber.* **1987**, *120*, 1645-1652. See also: Becker, G.; Grosser, G.; Uhl, W. *Z. Naturforsch.* **1981**, *36b*, 16-19.
16. Marinetti, A.; Bauer, S.; Ricard, L.; Mathey, F. *Organometallics* **1990**, *9*, 793-797.
17. Marinetti, A.; Mathey, F. *Angew. Chem.* **1988**, *100*, 1435-1437; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1382-1384.
18. Tables of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England. The data are available on request to the Director of CCDC by quoting the full literature reference of this paper.
19. Becker, G.; Hölderich, W. *Chem. Ber.* **1975**, *108*, 2484-2485.