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Modifying the Chemistry of the Phosphole Dienic System by α-Vinylation

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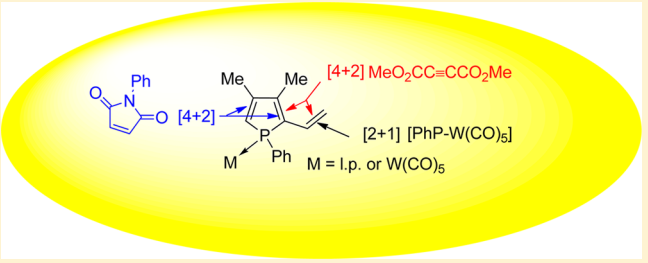
Supporting Information

ABSTRACT: 1-Phenyl-2-vinyl-3,4-dimethylphosphole (**4**) was prepared from the corresponding 2-carboxaldehyde via a Wittig reaction. The reaction of its P-$W(CO)_5$ complex **5** with [PhP-$W(CO)_5$] selectively takes place at the vinyl double bond and gives the corresponding phosphirane **6** as a mixture of two diastereomers. The reaction of **4** with *N*-phenylmaleimide involves the phosphole dienic system and gives the [4 + 2] 7-phosphanorbornene cycloadduct **7**. The reaction of **5** with dimethyl acetylenedicarboxylate either takes place at the phosphole dienic system and leads to the vinyl phthalate **10** with loss of the phosphorus bridge or involves the double bonds of the vinyl and one phosphole group to give the [4 + 2] cycloadduct **9**, which is oxidized in situ to give **11** with two epoxides and one ketone functionality. The products **6**, **7**, **9**, and **11** were characterized by X-ray crystal structure analysis.



In contrast to furans, thiophenes, and pyrroles, phospholes are essentially nonaromatic[1] as a result of the pyramidality of the heteroatom. Their weak aromatic stabilization energy[2] mainly results from a σ^*/π hyperconjugation between the exocyclic P−R bond and the dienic system. From a practical standpoint, this means that the chemistry of phospholes is mainly (but not exclusively) the superimposition of the classical chemistry of the phosphorus lone pair and the chemistry of the dienic system. On this basis, we wondered what could be the influence of a vinyl substituent on the α position of the ring. We expected a significant conjugation between the vinyl group and the diene, leading to a sizable modification of the chemistry of the phosphole ring. This is, indeed, the case to an unexpected extent, as reported hereafter. Quite surprisingly, even though a few α-alkenylphospholes have already been synthesized,[3] they have been studied as chromophores and the chemistry of their dienic system has not been investigated.

RESULTS AND DISCUSSION

In order to have a preliminary insight into what could be expected, we first performed comparative DFT calculations[4] on 1-methylphosphole (**1**) and 1-methyl-2-vinylphosphole (**2**) at the RB3LYP/6-311+G(d,p) level. A similar computational study on 1-methylphosphole has already been published.[5] The computed structure of **2** (Figure 1) suggests a significant conjugation between the vinyl group and the dienic system. Indeed, the vinyl group is coplanar with the diene and the C_α−vinyl bond is somewhat short at 1.451 Å and quite similar to the C−C intracyclic bond at 1.450 Å. Another criterion based on the alternation between C−C and C═C bonds also indicates that the diene is more delocalized in **2** than in **1** (mean alternation 0.089 Å in **2** vs 0.103 Å in **1**). In parallel, the phosphorus atom in **2** is more pyramidal than in **1**

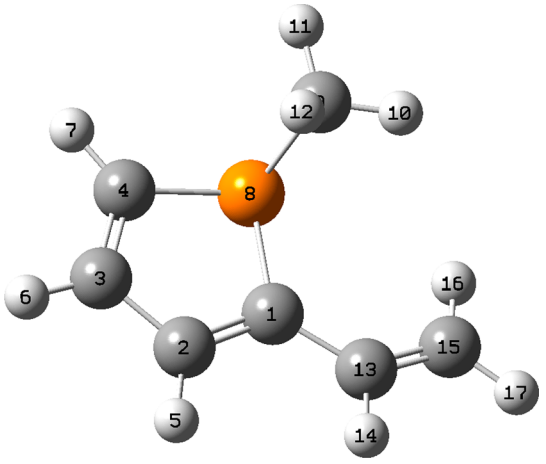


Figure 1. Computed structure of 1-methyl-2-vinylphosphole (**2**). Main distances (Å) and angles (deg): C1−P8 1.835, C4−P8 1.811, C9−P8 1.867, C1−C2 1.365, C2−C3 1.450, C3−C4 1.356, C1−C13 1.451, C13−C15 1.341; C1−P8−C4 90.36, C1−P8−C9 103.44, P8−C1−C13 125.93.

(∑C−P−C 297.9° vs 301.0°), suggesting less interaction between the heteroatom and the diene. A similar phenomenon had been noticed in α-acetylenic phospholes.[6] The picture is even more demonstrative when looking at the frontier orbitals (Kohn−Sham). The HOMO of **2** (Figure 2) is an antibonding combination of the vinyl π bond with the diene HOMO. It lies 0.46 eV higher in energy than the HOMO of **1**. Quite significantly,

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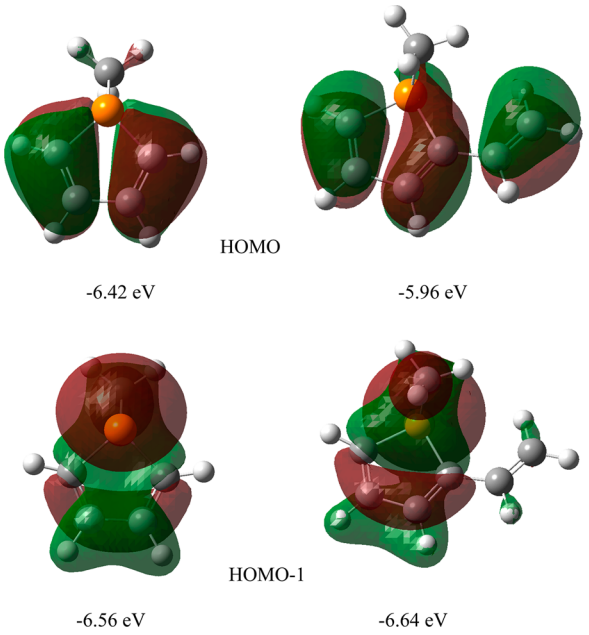
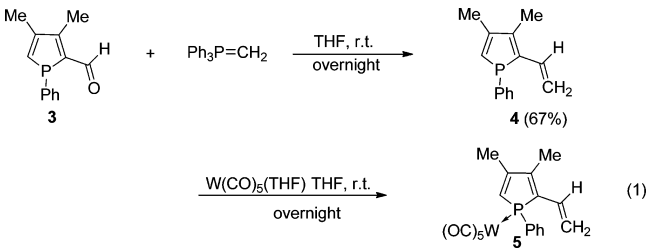


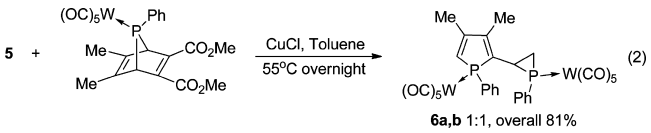
Figure 2. Computed frontier orbitals (Kohn−Sham) of 1-methylphosphole (**1**) and 1-methyl-2-vinylphosphole (**2**).

the energy of the lone pair orbital in **1** (HOMO-1) is practically not affected in **2**, confirming the very weak delocalization of the lone pair over the ring.

Since the perturbation by the vinyl substituent mainly takes place at the diene, we focused our experiments on the cycloaddition reactions. Our starting 2-vinylphosphole **4** was prepared by reaction of methylenetriphenylphosphorane with the aldehyde **3** (eq 1).



The structure of phosphole **4** was confirmed by X-ray crystal structure analysis of its P-W$(CO)_5$ complex **5** (Figure 3). The similarity between the computed structure of **2** and the experimental structure of **5** is obvious. The vinyl group is coplanar with the diene and directed toward phosphorus in both cases. We started our investigations on the reactivity of the unsaturated system of **4** and **5** by the reaction of the terminal phosphinidene complex [PhP-W$(CO)_5$] with **5** in comparison with its classical [1 + 2] cycloaddition with alkenes.[7] The reaction exclusively takes place at the vinyl substituent and proceeds in high yield (eq 2).



6a,b 1:1, overall 81%

It is clear that the condensation takes place at the vinyl double bond for steric reasons. The absence of steric hindrance explains why the two possible phosphirane diastereomers

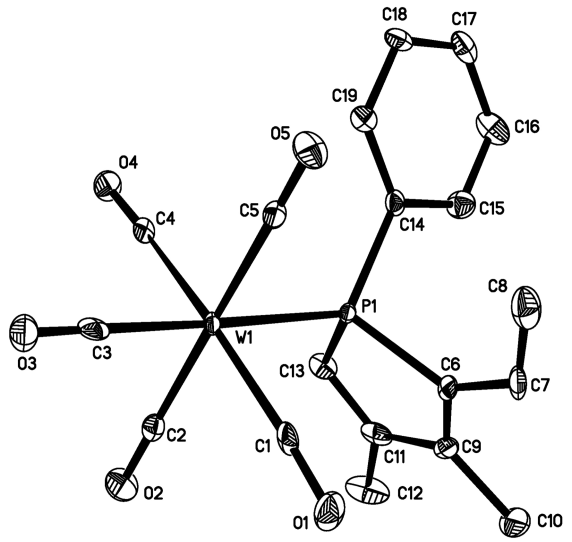
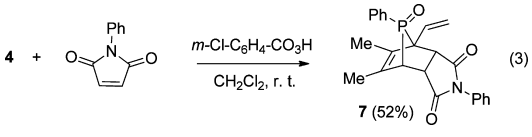


Figure 3. X-ray crystal structure of **5** . Main distances (Å) and angles (deg): C6−P1 1.806(7), C13−P1 1.794(8), C14−P1 1.834(8), C6−C9 1.359(11), C9−C11 1.449(12), C11−C13 1.340(11), C6−C7 1.459(11), C7−C8 1.317(13); C6−P1−C13 91.3(4), C6−P1−C14 105.1, P1−C6−C7 123.6(6).

($\delta(^{31}P)$ −155.5 (**6a**), −156.9 ppm (**6b**)) are obtained in equal amounts. The phosphirane **6a** was characterized by X-ray crystal structure analysis (Figure 4). The disruption of the conjugation between the exocyclic α substituent and the phosphole dienic system induces a lengthening of the phosphole−-substituent bond and an increase of the alternation within the diene (0.138 Å). The phosphole and phosphirane planes make an angle of 45°. The classical rearrangement of 2-vinylphosphiranes into phospholenes[7,8] does not proceed with **6**. Only decomposition products were observed upon heating.

Our next experiments concerned the cycloaddition reactions of *N*-phenylmaleimide with tervalent phospholes.[9] We could envisage two pathways, the first one involving the phosphole dienic system and the second one involving the vinyl substituent and the adjacent C═C double bond. The first route is favored by the locked cis conformation of the diene and the second one by the better accessibility of the double bonds but disfavored by the tendency of the diene to adopt the trans conformation. In practice, the preliminary experiments conducted in a NMR tube led to the endo adduct with the phosphole dienic system but, unexpectedly, the product was oxidized at P, and the cycloaddition had taken place on the side of P═O. It must be recalled that the reaction of *N*-phenylmaleimide with 1-phenyl-3,4-dimethylphosphole gives the nonoxidized adduct on the side of the P−Ph substituent.[9] We concluded that **4** itself is poorly reactive and was first oxidized to the unstable phosphole oxide[10] by atmospheric oxygen diffusing through the cap of the NMR tube to then give the cycloadduct, hence the stereochemistry. It is known that phosphole *P*-sulfides react by their P═S faces, and the phosphole oxides likely do the same. In order to confirm our hypothesis, we ran the oxidation of **4** at room temperature in the presence of *N*-phenylmaleimide and obtained the adduct **7** in 52% yield with only traces of the dimeric oxide of **4** (eq 3).



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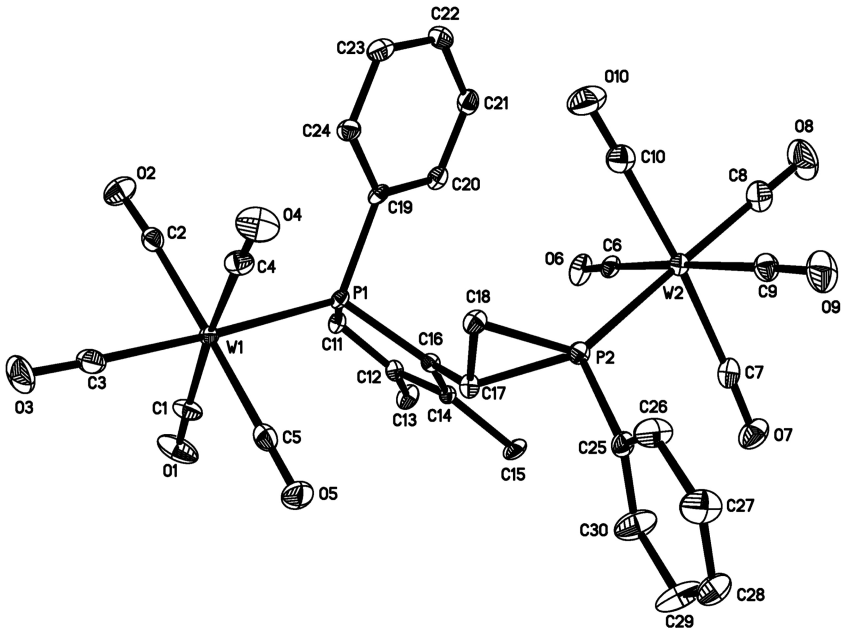
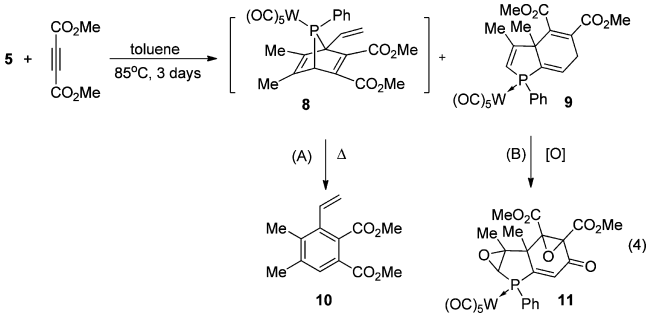


Figure 4. X-ray crystal structure of **6a**. Main distances (Å) and angles (deg): P1−C11 1.794(4), P1−C16 1.824(4), C11−C12 1.343(5), C12−C14 1.482(5), C14−C16 1.345(5), C16−C17 1.479(5), C17−C18 1.516(5), C17−P2 1.837(4), C18−P2 1.818(4); C11−P1−C16 91.21(17), C17−P2−C18 49.02(17).

The molecular structure of **7** was established by X-ray single-crystal analysis (Figure 5). The reaction of dimethyl acetylenedicarboxylate with **5** is more complex and proceeds very slowly. Two main reaction pathways have been identified (eq 4).



The first pathway (A) is the normal reaction pathway leading to the 7-phosphanorbornadienes,[11] which are used as phosphinidene precursors. The final product is the vinyl phthalate **10**. The second pathway (B) involves the vinyl group and the adjacent phosphole double bond and leads to the [4 + 2] cycloadduct **9**. The structure of **9** is shown in Figure 6. The former dienic unit C15−C17−C18−C20 is almost planar. The cyclohexadiene ring resulting from the cycloaddition is bent around its C15−C20 axis with an angle of 35.7°. The most puzzling observation is that a minute amount of **9** is oxidized in situ to give the final product **11** with two epoxidized double bonds and a ketonic group. Since the reaction is carried out in a sealed tube, the oxygen cannot come from the atmosphere. It probably comes from the excess dimethyl acetylenedicarboxylate, the transfer being mediated by a tungsten oxo species. Tungsten oxo species are known to be able to catalyze the epoxidation of olefins.[12] The structure of **11** was unambiguously established by an X-ray crystal structure analysis (Figure 7). The two epoxide rings are located on the P−phenyl side of the phosphole ring. If we admit that a tungsten oxo species is responsible for the epoxidation of the double bonds, it is clear that its steric bulk will

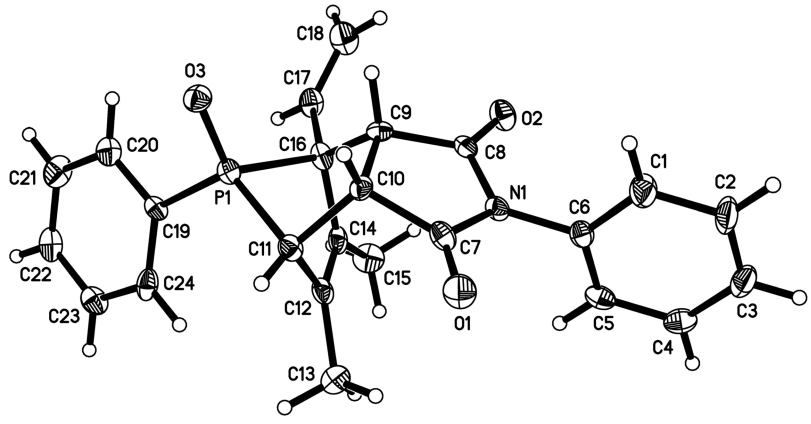


Figure 5. X-ray crystal structure of **7**. Main distances (Å) and angles (deg): P1−C11 1.831(6), P1−C16 1.872(5), C9−C10 1.544(7), C9−C16 1.564(7), C10−C11 1.567(7), C16−C17 1.495(8), C17−C18 1.302(8); C11−P1−C16 83.5(3).

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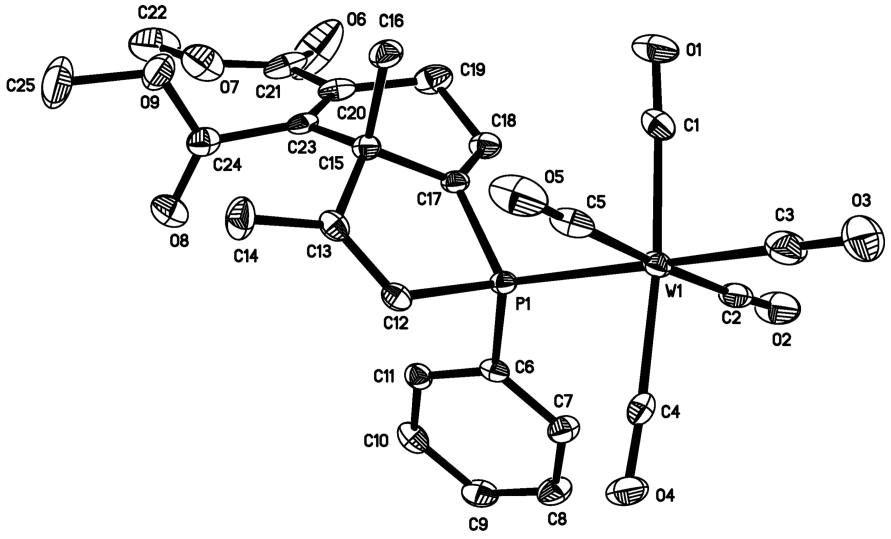

Figure 6. X-ray crystal structure of **9**. Main distances (Å) and angles (deg): P1−C12 1.798(3), P1−C17 1.809(3), C12−C13 1.330(5), C13−C15 1.537(4), C15−C17, 1.527(4), C17−C18 1.323(4), C18−C19 1.497(5), C19−C20 1.511(5), C20−C23 1.345(5), C23−C15 1.530(4); C12−P1−C17 89.97(15).

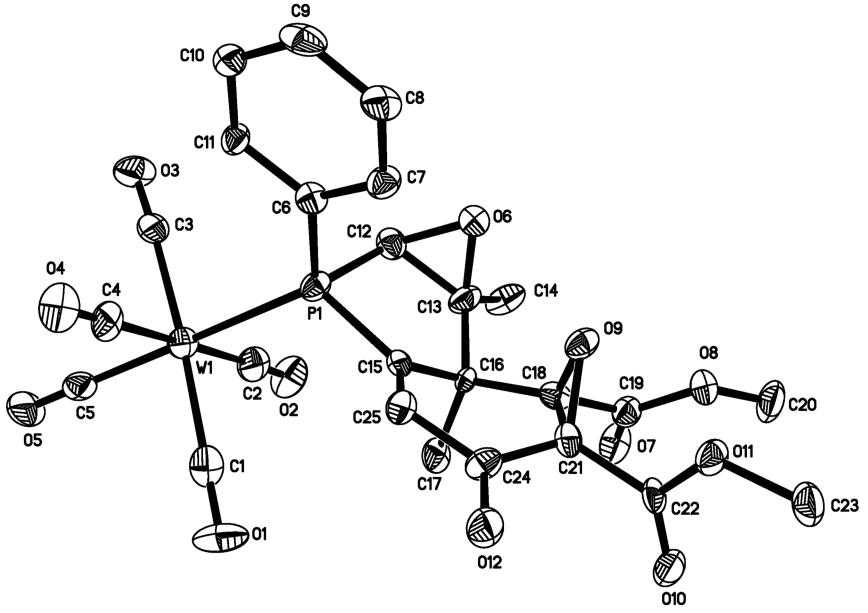

Figure 7. X-ray crystal structure of **11**. Main distances (Å) and angles (deg): P1−C12 1.810(10), P1−C15 1.820(10), C12−C13 1.494(14), C13−C16 1.543(13), C16−C15 1.527(13), C15−C25 1.330(14), C25−C24, 1.483(14), C24−O12 1.212(12), C24−C21 1.494(14), C21−C18 1.463(14), C16−C18 1.510(13), C12−O6 1.449(12), C13−O6 1.455(13), C18−O9 1.420(12), C21−O9 1.434(12); C12−O6−C13 61.9(6), C18−O9−C21 61.7(6), C12−P1−C15 89.5(5).

direct the epoxidation toward the less hindered side of the C═C bond: i.e., the side opposite to the $W(CO)_5$ complexing group for the phosphole double bond and the side opposite to the C17 methyl for the $MeO_2CC{=}CCO_2Me$ unit.

This preliminary work demonstrates that three pathways are possible for the cycloaddition reactions of **4** and **5**, the chosen pathway being dictated by the selected reagent. The selectivity is surprisingly high, thus allowing us to use this chemistry for the synthesis of new phosphorus ligands.

■ EXPERIMENTAL SECTION

Oven-dried glasswares (105 °C) were used and cooled under a nitrogen atmosphere. All reactions were carried out with distilled dry solvents and under an N_2 atmosphere. Silica gel (230−400 mesh) was used for the chromatographic separations. The phosphinidene precursor was synthesized as described in the literature.[11] NMR spectra were recorded on a JEOL ECA 400, a JEOL ECA 400 SL, or a Bruker BBFO2 400 MHz spectrometer. All spectra were recorded at 298 K. Proton decoupling was applied for ^{13}C and ^{31}P spectra. HRMS were obtained on a Water Q-Tof Premier MS. X-ray crystallographic analyses were performed on a Bruker X8 APEX CCD diffractometer or a Bruker Kappa CCD diffractometer.

1-Phenyl-2-vinyl-3,4-dimethylphosphole (4). *n*-BuLi (1.4 mL, 1.6 M in hexane, 2.2 mmol) was added dropwise into an oven-dried two-neck flask under N_2 containing methyltriphenylphosphonium iodide (0.8893, 2.2 mmol) suspended in THF (10 mL) at 0 °C. The reaction mixture was stirred at room temperature for 15 min. Subsequently, 3,4-dimethyl-1-phenylphosphole-2-carboxaldehyde (**3**;[13] 0.4335 g, 2.0 mmol) dissolved in THF (3 mL) was added. The reaction mixture was stirred overnight. The solvent was removed, and the crude product

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was purified using flash chromatography in degassed hexane. The phosphole was obtained in 67% yield (0.3715 g).

^{31}P NMR ($CDCl_3$): δ −3.31 ppm. ^{1}H NMR ($CDCl_3$): δ 2.08−2.09 (m, 3H, Me), 2.10−2.11 (m, 3H, Me), 4.97 (d, J_{H-P} = 10.6 Hz, 1H, =CH_2), 5.31 (d, J_{H-P} = 17.2 Hz, 1H, =CH_2), 6.35 (d, J_{H-P} = 39.7 Hz, 1H, =CH−P), 6.70−6.81 (m, 1H, =CH), 7.25−7.28 (m, 3H, Ph), 7.30−7.34 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 13.78 (d, J_{C-P} = 2.1 Hz, Me), 18.35 (d, J_{C-P} = 3.4 Hz, Me), 115.15 (d, J_{C-P} = 12.3 Hz, =CH_2), 127.92 (d, J_{C-P} = 1.1 Hz, P−CH), 128.68 (d, J_{C-P} = 8.0 Hz, Ph), 129.29 (s, Ph), 131.22 (d, J_{C-P} = 17.5 Hz, =CH), 133.29 (d, J_{C-P} = 11.8 Hz, P−C(Ph)), 133.61 (d, J_{C-P} = 19.4 Hz, Ph), 144.34 (s, P−C), 144.82 (d, J_{C-P} = 10.2 Hz, C-Me), 150.38 (d, J_{C-P} = 6.2 Hz, C-Me). Exact mass: calcd $C_{14}H_{16}P$, 215.0990; found, 215.0972.

1-Phenyl-2-vinyl-3,4-dimethylphosphole Pentacarbonyltungsten Complex 5. 1-Phenyl-2-vinyl-3,4-dimethylphosphole (**4**; 0.135 g, 0.63 mmol) dissolved in THF (3 mL) was added to $W(CO)_5$(THF) (0.7 mmol) and the mixture stirred overnight at room temperature. The solvent was removed under vacuum and the purification carried out by flash chromatography using hexane (0.3380 g, 99%).

^{31}P NMR ($CDCl_3$): δ 14.63 ppm (J_{P-W} = 221.0 Hz). ^{1}H NMR ($CDCl_3$): δ 2.18 (m, 6 H, Me), 5.16−5.23 (m, 2 H, =CH_2), 6.43 (d, $^2J_{H-P}$ = 36.8 Hz, 1H, =CH−P), 6.71−6.83 (m, 1H, C−CH=), 7.36−7.51 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$): δ 13.77 (d, $^3J_{C-P}$ = 8.4 Hz, Me), 17.71 (d, $^3J_{C-P}$ = 10.5 Hz, Me), 118.97 (d, $^3J_{C-P}$ = 7.2 Hz, =CH_2), 128.65 (d, $^2J_{C-P}$ = 14.4 Hz, C−CH=), 129.21 (d, J_{C-P} = 10.5 Hz, Ph), 129.61 (d, J_{C-P} = 38.6 Hz, P−C(Ph)), 130.95 (d, J_{C-P} = 44.1 Hz, P−CH=), 131.04 (d, J_{C-P} = 2.3 Hz, Ph), 132.48 (d, J_{C-P} = 13.0 Hz, Ph), 142.40 (d, J_{C-P} = 42.5 Hz, P−C), 145.90 (d, J_{C-P} = 14.7 Hz, C-Me), 150.00 (d, J_{C-P} = 7.5 Hz, C-Me), 196.61 (d, J_{C-P} = 6.4 Hz, $W(CO)_5$ *cis* C=O), 198.83 (d, J_{C-P} = 19.3 Hz, $W(CO)_5$ *trans* C=O). Exact mass: calcd $C_{19}H_{15}O_5PW$, 538.0166; found, 538.0166.

Phosphirane Complexes 6a,b. Complex **5** (0.199 g, 0.37 mmol), CuCl (0.019 g, 0.19 mmol), and 7-phenyl-7-phosphanorbornadiene tungsten complex[11] (0.726 g, 1.1 mmol) were dissolved in toluene. The mixture was heated to 55 °C for 1 day in a sealed tube. Solvent was removed, followed by purification by chromatography with a 1/4 mixture of dichloromethane and hexane as the eluent. Isomer A (0.074 g, 41%) was eluted before isomer B (0.072 g, 40%).

Isomer A. ^{31}P NMR ($CDCl_3$): δ −155.46 (d, J_{P-P} = 18 Hz, J_{P-W} = 268.7 Hz), 22.11 (d, J_{P-P} = 18 Hz, J_{P-W} = 216.7 Hz). ^{1}H NMR (CD_2Cl_2): δ 1.21−1.27 (m, 1H, CH_2), 2.24−2.30 (m, 1H, CH_2), 2.28 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.74 (m, 1H, CH), 6.65 (d, J_{P-H} = 36.0 Hz, 1H, =CH), 7.42−7.46 (m, 6H, Ph), 7.51−7.56 (m, 2H, Ph), 7.62−7.67 (m, 2H, Ph). ^{13}C NMR (CD_2Cl_2): δ 15.37 (d, J_{P-C} = 8.8 Hz, CH_3), 15.97 (dd, $^1J_{P-C}$ = 11.0 Hz, $^3J_{P-C}$ = 4.8 Hz, CH_2), 18.22 (d, J_{P-C} = 10.5 Hz, CH_3), 26.49 (pseudo t, J_{P-C} = 34.5 Hz, CH), 128.76 (d, J_{P-C} = 37.0 Hz, P−C(Ph)), 129.55 (d, J_{P-C} = 9.9 Hz, Ph), 129.76 (d, J_{P-C} = 10.5 Hz, Ph), 130.76 (d, J_{P-C} = 49.1 Hz, =CH), 131.58 (d, J_{P-C} = 1.9 Hz, Ph), 131.79 (d, J_{P-C} = 12.0 Hz, Ph), 132.43 (d, J_{P-C} = 2.4 Hz, Ph), 134.01 (d, J_{P-C} = 13.7 Hz, Ph), 136.13 (d, J_{P-C} = 29.3 Hz, P−C(Ph)), 140.78 (d, J_{P-C} = 39.5 Hz, P−C=), 150.09 (dd, J_{P-C} = 5.7 Hz, J_{P-C} = 17.3 Hz, C−Me), 152.71 (dd, J_{P-C} = 2.5 Hz, J_{P-C} = 7.9 Hz C−Me), 195.97 (d, J_{C-P} = 8.1 Hz, $W(CO)_5$ *cis* C=O), 197.17 (d, J_{C-P} = 6.3 Hz, $W(CO)_5$ *cis* C=O), 197.78 (d, J_{C-P} = 31.9 Hz, $W(CO)_5$ *trans* C=O), 198.86 (d, J_{C-P} = 19.0 Hz, $W(CO)_5$ *trans* C=O). Exact mass: calcd $C_{30}H_{20}O_{10}P_2W_2Na$, 992.9448; found, 992.9495.

Isomer B. ^{31}P NMR (CD_2Cl_2): δ −156.94 (d, J_{P-P} = 5.7 Hz, J_{P-W} = 261.1 Hz), 20.29 (d, J_{P-P} = 5.7 Hz, J_{P-W} = 216.7 Hz). ^{1}H NMR (CD_2Cl_2): δ 1.86−1.93 (m, 2H, CH_2), 2.17 (d, J_{P-H} = 0.9 Hz, 3H, CH_3), 2.29 (d, J_{P-H} = 1.0 Hz, 3H, CH_3), 2.66 (pseudo t, J_{P-H} = 19.6 Hz, 1H, CH), 6.38 (d, J_{P-H} = 36.0 Hz, 1H, =CH), 6.80−6.85 (m, 2H, Ph), 7.01−7.15 (m, 6H, Ph), 7.24−7.34 (m, 2H, Ph). ^{13}C NMR (CD_2Cl_2): δ 14.93−15.07 (m, CH_2), 15.44 (d, J_{P-C} = 8.9 Hz, CH_3), 18.04 (d, J_{P-C} = 10.5 Hz, CH_3), 27.71−28.07 (m, CH), 127.46 (d, J_{P-C} = 37.2 Hz, P−C(Ph)), 129.52 (d, J_{P-C} = 10.2 Hz, Ph), 129.74 (d, J_{P-C} = 10.4 Hz, Ph), 130.52 (d, J_{P-C} = 47.1 Hz, =CH), 130.83 (d, J_{P-C} = 1.9 Hz, Ph), 131.20 (d, J_{P-C} = 30.5 Hz, P−C(Ph)), 131.42 (d, J_{P-C} = 2.3 Hz, Ph), 132.27 (d, J_{P-C} = 12.3 Hz, Ph), 133.23 (d, J_{P-C} = 13.6 Hz, Ph), 139.99 (dd, J_{P-C} = 6.8 Hz, J_{P-C} = 38.8 Hz, P−C=), 148.79 (dd, J_{P-C} = 4.7 Hz, J_{P-C} = 17.1 Hz, C−Me), 151.76 (d, J_{P-C} = 8.0 Hz, C−Me), 196.17 (d, J_{C-P} = 8.0 Hz, $W(CO)_5$ *cis* C=O), 197.06 (d, J_{C-P} = 6.6 Hz, $W(CO)_5$ *cis* C=O), 198.53 (d, J_{C-P} = 31.0 Hz, $W(CO)_5$ *trans* C=O), 198.73 (d, J_{C-P} = 19.0 Hz, $W(CO)_5$ *trans* C=O). Exact mass: calcd $C_{30}H_{20}O_{10}P_2W_2Na$, 992.9448; found, 992.9495.

7-Phosphanorbornene Oxide 7. *m*-Chloroperoxybenzoic acid (0.0814 g, 70% in H_2O, 0.33 mmol) was dissolved in 5 mL of dichloromethane and dried over $MgSO_4$. It was filtered into an addition funnel attached to a two-neck flask containing 2-vinylphosphole **4** (0.0443 g, 0.33 mmol) and *N*-phenylmaleimide (0.0629 g, 0.36 mmol) dissolved in 2 mL of dichloromethane. Then, *m*-CPBA solution was added dropwise into the reaction mixture at room temperature for 4 h. The crude product was purified by chromatography with a 2/3 mixture of hexane and ethyl acetate as the eluent. Oxide **7** was obtained (0.0692 g, 52%).

^{31}P NMR (CH_2Cl_2): δ 74.4. ^{1}H NMR (CD_2Cl_2): δ 1.65 (s, 3H, Me), 1.78 (s, 3H, Me), 3.54−3.57 (m, 1H, CH), 4.07−4.14 (m, 2H, CH), 5.52−5.55 (m, 1H, =CH_2), 5.68−5.73 (m, 1H, =CH_2), 6.14−6.24 (m, 1H, =CH), 7.06−7.08 (m, 2H, Ph), 7.38−7.58 (m, 8H, Ph). ^{13}C NMR (CD_2Cl_2): δ 13.27 (d, J_{P-C} = 3.0 Hz, CH_3), 16.04 (d, J_{P-C} = 4.4 Hz, CH_3), 45.42 (d, J_{P-C} = 12.4 Hz, CH), 48.46 (d, J_{P-C} = 87.3 Hz, P−CH), 48.7 (d, J_{P-C} = 8.3 Hz, CH), 60.48 (d, J_{P-C} = 66.0 Hz, P−C),121.23 (d, J_{P-C} = 10.1 Hz, =CH_2), 127.31 (s, Ph), 129.25 (d, J_{P-C} = 8.9 Hz, P−C(Ph)), 129.28 (s, Ph), 129.42 (d, J_{P-C} = 6.7 Hz, Ph), 129.62 (d, J_{P-C} = 6.1 Hz, =CH), 129.81 (s, Ph), 130.44 (d, J_{P-C} = 8.8 Hz, =C), 132.59 (s, Ph), 132.79 (d, J_{P-C} = 8.0 Hz, Ph), 133.15 (d, J_{P-C} = 2.7 Hz, Ph), 133.84 (d, J_{P-C} = 10.8 Hz, =C), 174.97 (d, J_{P-C} = 13.4 Hz, C=O), 175.63 (d, J_{P-C} = 14.1 Hz, C=O). Exact mass: calcd $C_{24}H_{23}O_3PN$, 404.1416; found, 404.1434.

Reaction of 5 with Dimethyl Acetylenedicarboxylate. Complex **5** (0.116 g, 0.22 mmol) was dissolved in 2 mL of toluene, and dimethyl acetylenedicarboxylate (0.08 mL, 0.66 mmol) was added. The reaction tube was sealed and heated at 90 °C for 3 days. Two new peaks were observed in the crude reaction mixture at 2.87 ppm (J_{P-W} = 233.5 Hz) and 21.0 ppm (J_{P-W} = 218.9 Hz) with the presence of starting material at 14 ppm. Purification was performed by gradient chromatography, with a 1/4 mixture of dichloromethane and hexane as the eluent to 100% dichloromethane. A mixture of products **9** and **11** was first eluted, followed by compound **10** (0.0175 g of colorless oil, 43.8%). Compounds **9** and **11** were separated by PTLC, with a 4/1 mixture of dichloromethane and hexane as the eluent. A 0.013 g portion of pale yellow solid **9** was obtained (12%), while compound **11** was recovered as a yellow oil (0.0029 g, 2%).

Compound 9. ^{31}P NMR (CD_2Cl_2): δ 2.73 (J_{P-W} = 234.1 Hz). ^{1}H NMR (CD_2Cl_2): δ 1.53 (s, 3H, Me), 2.04 (s, 3H, Me), 3.07 (m,1H, CH_2), 3.33−3.41 (m, 1H, CH_2), 3.70 (s, 3H, OMe), 3.82 (s, 3H, OMe), 6.04 (d, $^2J_{H-P}$ = 33.6 Hz, 1H, P−CH=), 6.28−6.32 (m, 1H, =CH), 7.38−7.58 (m, 5H, Ph). ^{13}C NMR (CD_2Cl_2): δ 17.27 (d, J_{C-P} = 10.0 Hz, Me), 27.11 (s, Me), 28.97 (d, J_{C-P} = 10.1 Hz, CH_2), 52.84 (s, OMe), 52.95 (s, OMe), 55.75 (d, J_{C-P} = 13.5 Hz, C−Me), 125.24 (d, J_{C-P} = 46.8 Hz, P−CH=), 128.54 (s, C), 129.30 (d, J_{C-P} = 10.1 Hz, Ph), 131.11 (d, J_{C-P} = 2.2 Hz, Ph), 132.39 (d, J_{C-P} = 13.7 Hz, Ph), 133.84 (d, J_{C-P} = 12.9 Hz, =CH), 137.72 (d, J_{C-P} = 34.1 Hz, P−C(Ph)), 147.42 (d, J_{C-P} = 41.7 Hz, P−C=), 148.97 (s, C), 156.63 (s, C), 165.80 (s, CO_2Me), 169.21 (s, CO_2Me), 197.44 (d, J_{C-P} = 7.0 Hz, $W(CO)_5$ *cis* C=O), 200.03 (d, J_{C-P} = 20.1 Hz, $W(CO)_5$ *trans* C=O). Exact mass: calcd $C_{25}H_{21}O_9PW$, 680.0433; found, 680.0413.

Compound 11. ^{31}P NMR (CD_2Cl_2): δ 21.39. Exact mass: calcd $C_{25}H_{19}O_{12}PW$, 726.0124; found, 726.0128.

Compound 10. ^{1}H NMR ($CDCl_3$): δ 2.24 (s, 3H, Me), 2.32 (s, 3H, Me), 3.85 (s, 3H, OMe), 3.87 (s, 3H, OMe), 5.33 (dd, $J_{(H-H)}$ = 18.0 Hz, $J_{(H-H)}$ = 1.6 Hz, 1H, CH_2), 5.49 (dd, $J_{(H-H)}$ = 12.8 Hz, $J_{(H-H)}$ = 1.6 Hz, 1H, CH_2), 6.70−6.78 (m, 1H, =CH), 7.73 (s, 1H, Ph). ^{13}C NMR (CD_2Cl_2): δ 16.96 (Me), 20.65 (Me), 52.48 (OMe), 52.51 (OMe), 121.00 (CH_2), 124.79 (Ph), 130.28 (C−H(Ph)), 133.08 (Ph), 134.26 (CH), 136.78 (Ph), 138.03 (Ph), 140.45 (Ph), 166.42 (CO_2Me), 170.09 (CO_2Me). Exact mass: calcd $C_{14}H_{17}O_4$, 249.1127; found, 249.1141.

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■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, and CIF and xyz files giving X-ray crystal structure analyses of compounds **5**, **6a**, **7**, **9**, and **11**, all computed molecule **2** Cartesian coordinates in a format for convenient visualization, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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