# Diastereoselective Formation of Complexed Methylenediphosphiranes

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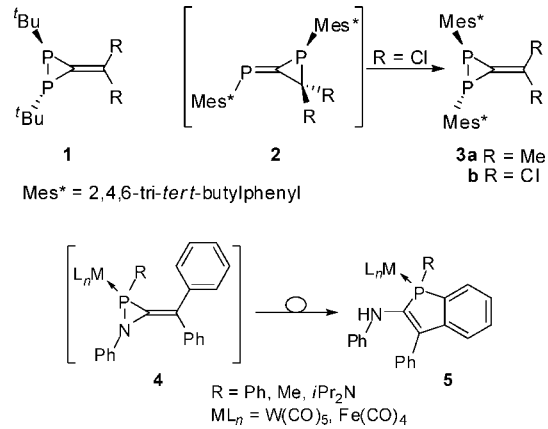
Stable *syn*-substituted methylenediphosphirane complexes are obtained from the reaction of transient, electrophilic phosphinidenes [R−P═W(CO)$_5$] (R = Me, Ph), thermally generated from the corresponding benzophosphepines, with 1-phosphaallene. A DFT analysis at the B3PW91/6-31G(d) level of theory reveals that the high diastereoselectivity of this reaction results from the preferred negative activation energy for *syn* cyclization of the P,P-ylide intermediates.

## Introduction

Although the all-carbon methylenecyclopropanes are heavily scrutinized for their use as radical probes[1] and as monomers in (co)polymerization[2] and multicomponent reactions[3] and their biological activity,[4,5] the synthesis of the phosphorus-containing analogues is quite challenging. Undoubtedly, the inherent strain that underlies the applicability of the hydrocarbon is more readily released due to the weaker phosphorus−carbon bond, but also the lack of synthetic methodologies limits their access. Indeed, merely three methylenediphosphiranes have been reported.[6] Baudler et al. synthesized **1** by a condensation route,[7] while Koenig and co-workers obtained diphosphirane **3a** by isopropylidene carbene addition to a *trans*-diphosphene.[8] Yoshifuiji et al. synthesized **3b** by rearrangement of **2**, which is the product of the dichlorocarbene addition to a 1,3-diphosphaallene.[9] Heteroallenes are especially interesting because of their accessibility and reactivity.[10] For example, ketenimines (RN═C═CR$_2$) react with phosphinidene complexes [R−P═ML$_n$] (ML$_n$ = W(CO)$_5$ and Fe(CO)$_4$)[11] to give methyleneazaphosphiranes **4**, which undergo a [1,5]-sigmatropic rearrangement and a H-shift to afford 2-aminophosphindoles **5**.[12]




Electrophilic phosphinidene complexes[11] are ideal reagents to synthesize three-membered phosphacycles and potentially also the P-analogues of methylenecyclopropanes.[13] These carbene-like transients are typically generated by thermal fragmentation of 7-phosphanorbornadiene **6**,[14] but the phosphacycles, like **4**, can rearrange at the required reaction temperature of 110 °C or decompose,[14b,c,15] while the CuCl-catalyzed fragmentation at

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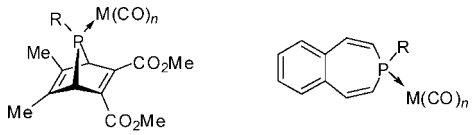
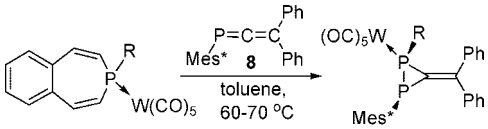
≤55 °C generates presumably [R−P(Cl)M(CO)$_5$]-Cu-L (L = alkene or solvent), which is more sensitive toward steric




M = Cr, Mo, W; R = e.g. Me, Ph

congestion and therefore can react differently.[16] A powerful alternative to **6** is the readily accessible 3*H*-3-benzophosphepine complex **7**, which generates terminal phosphinidene complexes at modest reaction temperatures (≥60 °C) without the use of a catalyst.[17] Here, we illustrate that stable methylenediphosphiranes result by reacting **7** with a phosphaallene. DFT calculations are presented to provide insight into this reaction.[3]

**Scheme 1. Synthesis of Methylenediphosphiranes 9**




**7a**: R = Me
**b**: R = Ph

## Results and Discussion

Reaction of the terminal phosphinidene complexes [R−P═W(CO)$_5$], generated in situ at 60−70 °C from 3*H*-3-benzophosphepine complexes **7a**,**b** (R = **a**, Me; **b**, Ph),[17] with 1-phosphaallene **8**[18] resulted in the formation of the W(CO)$_5$-complexed methylenediphosphiranes **9a** and **9b** as sole products in respectively 50% and 55% isolated yield after column chromatography and crystallization (Scheme 1). The products are air stable (mp **9a**, 162; **9b**, 200 °C) and show no signs of decomposition after storage for weeks at room temperature.

The synthesis of **9** is remarkably selective, yielding only one of the two possible diastereomers, as evidenced by the single AB spin system in the $^{31}$P NMR (**9a**: $\delta$ $^{31}$P −111.0, $^1J$(P,W) = 249.4 Hz; −134.5 ppm. **9b**: $\delta$ $^{31}$P −109.8, $^1J$(P,W) = 256.4 Hz; −106.0 ppm). *anti*-Configured diphosphiranes have $^1J$(P,P) coupling constants on the order of 150−210 Hz,[19] but **9** displays significantly smaller ones (**9a**, 72.9 Hz; **9b**, 77.8 Hz). Therefore **9** is likely to have a *syn* configuration in which the P-substituent R is on the same side of the PPC ring as the Mes* group (2,4,6-tri-*tert*-butylphenyl).[20] Single-crystal X-ray analysis established unequivocally the *syn* configuration for diphosphiranes **9a** and **9b** (Figure 1 ), with both having similar C15−P1−P2−C16/21 torsion angles (**9a**, −4.65(12)°; **9b**, 5.03(7)°) and comparable bond lengths and angles. **9b** has an interplanar angle of 19.4°, meaning that the rings are slightly tilted with respect to each other; the distance between the centers of both rings is 3.7451(10) Å. It is interesting to note that the exocyclic double bonds of **9a** and **9b** bend out of plane with P1−C1−C2−C3 torsion angles of −27.5(4)° and 27.1(2)°, respectively.

Methylenediphosphirane **9b** was hardly formed by thermal degradation of 7-phosphanorbornadiene **6**[21] (R = Ph, M = W) in the presence of **8**. After complete consumption of **6** (16 h) at 110 °C only 17% of **9b** was observed in the $^{31}$P NMR spectrum due to its instability under the reaction conditions. At 55 °C, using CuCl as a catalyst, product formation was not observed, likely due to complexation of CuCl to the phosphaallene.[22] Evidently, complexed 3*H*-3-benzophosphepine **7** offers an advantage in synthesizing thermally labile heterocycles.[23]

The diastereoselective formation of **9** was examined at the B3PW91/6-31G(d) (LANL2DZ for W) level of theory.[24] To keep the calculations manageable, model structures were used (labeled ′) in which the exocyclic double bond carries no substituents and the uncomplexed phosphorus a Ph instead of the bulky Mes* group. The discussion focuses mostly on the formation of **9a**, as **9b** shows similar behavior.

The first step in the reaction is likely to be the addition of [R−P═W(CO)$_5$] to the phosphorus lone pair of **8′**, resulting in *syn* and *anti* P,P-ylides **10′**[22,25] as the initial (kinetic) products (*syn*-**10a′**, $\Delta E$ = −15.4; *anti*-**10a′**, −15.1 kcal·mol$^{-1}$; Figure 2, all energies are relative to *syn*-**10a′**) in analogy to the formation of the well-documented P,N-ylides.[12,26] Due to the small energy difference between *syn* and *anti* P,P-ylides **10′** ($\Delta E$ = **10a′**, 0.3; **10b′**, 0.7 kcal·mol$^{-1}$), they will readily interconvert via a simple rotation around the P1−P2 bond, of which the clockwise motion (**TS2**; $\Delta E^{\ddagger}$ = **10a′**, 2.6; **10b′**, 2.3 kcal·mol$^{-1}$) is favored over the counter-clockwise motion (**TS1**; $\Delta E^{\ddagger}$ = **10a′**, 5.2; **10b′**, 4.3 kcal·mol$^{-1}$; Figure 2).

Ring closure of *syn* P,P-ylide **10a′** to *syn*-**9a′** requires 6.1 kcal·mol$^{-1}$, whereas the corresponding conversion of *anti*-**10a′** to *anti*-**9b′** has a slightly higher barrier (7.4 kcal·mol$^{-1}$; Figure 3).[27] The difference in energy barriers for the *syn* and *anti* ring closure is more pronounced for the phenyl-substituted derivatives (**10b′** → **9b′**) and amounts to 4.9 and 8.0 kcal·mol$^{-1}$ for the *syn* and *anti* conformers, respectively (Figure 3). It seems that steric congestion plays a role; that is, the difference in negative activation energies is 1.3 kcal·mol$^{-1}$ for the methyl-substituted phosphinidene and 3.1 kcal·mol$^{-1}$ for the phenyl derivative. To further explore this effect, we replaced the phosphaallene phenyl substituent of **9a′** for the much bulkier mesityl group. Indeed the difference in energy barriers increased from 1.3 to 2.1 kcal·mol$^{-1}$ (Table 1). The sterically still more

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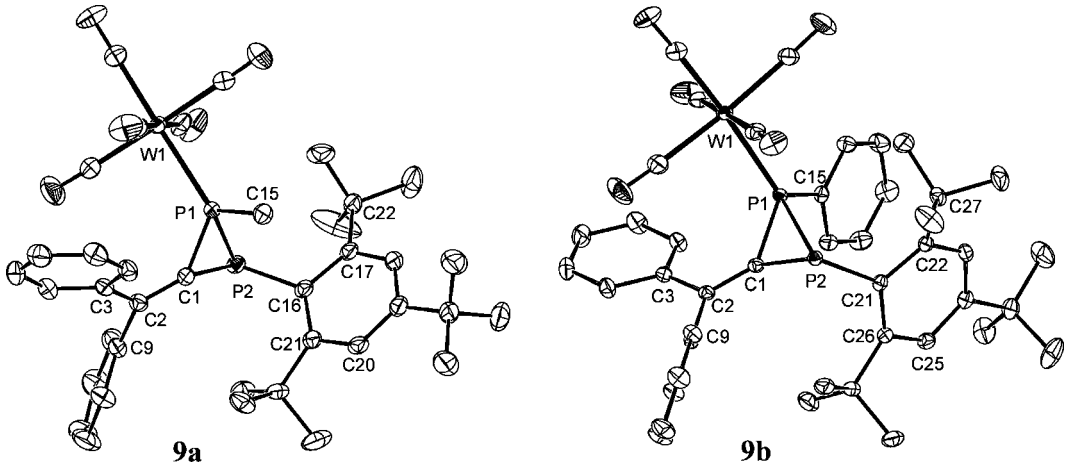


**Figure 1.** Displacement ellipsoid plot (50% probability) of **9a** and **9a**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [deg], and torsion angles [deg] for **9a** and **9b** (in square brackets): P1−P2 2.2260(8) [2.2399(5)], P1−C1 1.786(2) [1.7884(15)], P1−C15 1.827(2) [1.8134(15)], P1−W1 2.4977(6) [2.5052(4)], P2−C1 1.840(2) [1.8357(15)], C1−C2 1.353(3) [1.354(2)]; P1−P2−C1 51.04(7) [50.88(5)], P2−P1−C1 53.22(8) [52.78(5)], P1−C1−P2 75.74(9) [76.34(6)], P2−P1−W1 123.72(3) [120.500(19)], P2−P1−C15 109.59(9) [110.06(5)], C1−P1−C15 109.60(11) [108.25(7)]; C15−P1−P2−C16[C21] −4.65(12) [5.03(7)], P1−C1−C2−C3 −27.5(4) [27.1(2)], P2−C1−C2−C9 17.8(4) [−12.5(3)], ∑(P1) = 272.41 [271.09], ∑(P2) = 260.11 [261.65].

demanding supermesityl (Mes*) substituent that is used in the experiment is expected to have an even more profound effect, thereby dictating the selective ring closure of the initially formed P,P-ylide. The $W(CO)_5$ group gives a complementary steric effect on rotating over the allene during ring closure of *anti*-**10a′**. Without the $W(CO)_5$ group (labeled by ″) the formation of *anti*-**9a″** ($\Delta E^{\ddagger}$ = 9.1 kcal·mol$^{-1}$) is favored over *syn*-**9a″** ($\Delta E^{\ddagger}$ = 11.7 kcal·mol$^{-1}$; Table 1), which is in line with the reported preference for the metal-free *anti*-methylenediphosphiranes (**5**, **7**).

## Conclusions

Transient electrophilic phosphinidene complex [R−P=$W(CO)_5$] (R = Me, Ph), generated in situ only from 3*H*-3-benzophosphepine complex **7** at 60−70 °C, reacts with 1-phosphaallene to afford stable complexed methylenediphosphirane **9**. Calculations at the B3PW91/6-31G(d) (LANL2DZ for W) level of theory suggest that the diastereoselective formation of only the *syn* isomer **9** results from the favored negative activation energy for *syn* ring closure of the interconverting *syn* and *anti* P,P-ylides **10**, with the bulky Mes* and $W(CO)_5$ groups playing a prominent role.

## Experimental Section

**Computations.** All density functional theory calculations (B3PW91) were performed with the Gaussian03 suite of programs,[28] using the LANL2DZ basis set and pseudopotentials for tungsten and the 6-31G(d) basis set for all other atoms. The nature of each structure was confirmed by frequency calculations. Intrinsic reaction coordinate (IRC) calculations were performed to ascertain the connection between reactant and product.

**General Procedures.** All syntheses were performed with the use of Schlenk techniques under an atmosphere of dry nitrogen. Solvents were used as purchased, except for toluene, which was freshly distilled under nitrogen from sodium. NMR spectra were recorded at 300.2 K on a Bruker Advance 250 ($^1$H, $^{13}$C, $^{31}$P; 85% $H_3PO_4$) or a Bruker Advance 400 ($^1$H, $^{13}$C) and referenced internally to residual solvent resonances ($CDCl_3$: $^1$H, $\delta$ 7.25; $^{13}$C{$^1$H}, $\delta$ 77.0). IR spectra were recorded on a Shimadzu FTIR-84005 spectrophotometer. Fast atom bombardment (FAB) mass spectrometry was carried out using a JEOL JMS SX/SX 102A four-sector mass spectrometer, coupled to a JEOL MS-MP9021D/UPD system program. Samples were loaded in a matrix solution (3-nitrobenzyl alcohol) onto a stainless steel probe and bombarded with xenon atoms with an energy of 3 keV. During the high-resolution FAB-MS measurements a resolution power of 10 000 (10% valley definition) was used. Elemental analysis of **9a** was performed by the Microanalytical Laboratory of the Laboratorium für Organische Chemie, ETH Zürich. Melting points were measured on samples in unsealed capillaries and are uncorrected. 5,6-Dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene pentacarbonyltungsten(0) (**6**),[21] 3*H*-3-benzophosphepine complexes **7a**,**b**,[17] and phosphaallene **8**[18] were synthesized according to literature procedures.

**1-Methyl-2-[2,4,6-tri-*tert*-butylphenyl]-3-diphenylmethylene-1,2-diphosphirane Pentacarbonyltungsten(0) (9a).** A solution of phosphaallene **8** (318.8 mg, 0.57 mmol) and 3-methyl-3*H*-3-benzophosphepine complex **7a** (239.0 mg, 0.48 mmol) in toluene (20 mL) was heated at 70 °C for 62 h. Evaporation to dryness and chromatography of the residue over silica with pentane as eluent ($R_f$ = 0.35) and subsequent crystallization from pentane at −20 °C to remove the remaining phosphaallene yielded diphosphirane **9a** (218.5 mg, 55%) as yellow blocks. Crystals suitable for single-crystal X-ray structure determination were obtained from pentane at −20 °C. Mp: 162 °C (dec). $^{31}$P{$^1$H} NMR (101.3 MHz, $CDCl_3$): $\delta$ −111.0 (d, $^1J$(P,P) = 72.9 Hz, $^1J$(P,W) = 249.4 Hz; *P*$CH_3$), −134.5 (d, $^1J$(P,P) = 72.9 Hz; *P*Mes*). $^1$H NMR (250.1 MHz, $CDCl_3$): $\delta$ 0.70 (d, $^2J$(H,P) = 6.8 Hz, 3H; PC$H_3$), 1.14 (bs, 9H; *o*-C($CH_3$)$_3$-ArP), 1.32 (s, 9H; *p*-C($CH_3$)$_3$-ArP), 1.75 (bs, 9H;

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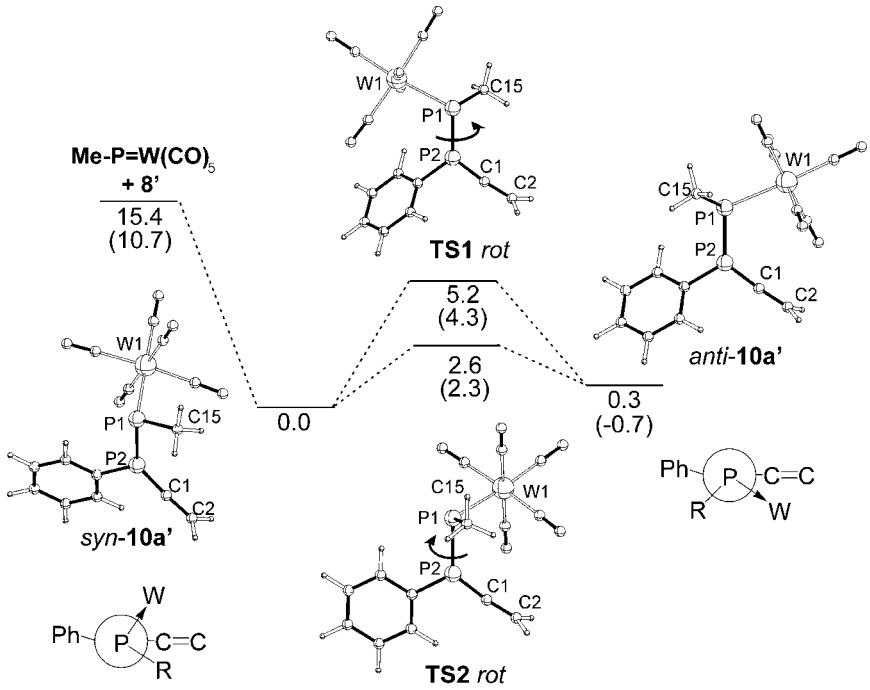



**Figure 2.** Relative B3PW91/6-31G(d) (LANL2DZ for W) energies (ZPE corrected, in kcal·mol$^{-1}$) for the interconversion of P,P-ylide *syn*-**10a′** into *anti*-**10a′**. The relative energies for the Ph derivatives are given in parentheses. Selected bond lengths [Å] and torsion angles [deg] of *syn*-**10a′**: P1−C1 3.404 (3.424), P1−P2 2.147 (2.155); C1−P2−P1−C15 −5.4 (−17.1); **TS1***rot*: P1−C1 3.298 (3.290), P1−P2 2.181 (2.183), C1−P2−P1−C15 74.1 (77.5); **TS2***rot*: P1−C1 3.431 (3.439), P1−P2 2.180 (2.186), P2−C1 1.628 (1.626); C1−P2−P1−C15 −70.2 (−74.5); *anti*-**10a′**: P1−C1 3.370 (3.364), P1−P2 2.152 (2.154), C1−P2−P1−C15 −137.1 (−137.9).

*o*-C(C*H*$_3$)$_3$-ArP), 7.10−7.45 (m, 11H; Ar*H*), 7.91 (bs, 1H; *m*-PAr*H*). $^{13}$C{$^1$H} NMR (62.9 MHz, CDCl$_3$): $\delta$ 17.1 (d, $^1J$(C,P) = 5.0 Hz; P*C*H$_3$), 31.3 (s; *p*-C(*C*H$_3$)$_3$-ArP), 32.1 (bs; *o*-C(*C*H$_3$)$_3$-ArP), 34.1 (d, $^4J$(C,P) = 12.1 Hz; *o*-C(*C*H$_3$)$_3$-ArP), 34.8 (s; *p*-*C*(CH$_3$)$_3$-ArP), 37.7 (bs; *o*-*C*(CH$_3$)$_3$-ArP), 38.9 (bs; *o*-*C*(CH$_3$)$_3$-ArP), 122.1 (s; *p*-Ar*C*H), 122.4 (s; *p*-Ar*C*H), 128.3 (bs; *m*-PAr*C*H), 128.4 (s; *m*-Ar*C*H), 129.8 (s; *o*-Ar*C*H), 130.2 (s; *m*-Ar*C*H), 130.5 (s; *o*-Ar*C*H), 130.9 (bs; *m*-PAr*C*H), 132.4 (d, $^1J$(C,P) = 202.7 Hz; *ipso*-PAr*C*$_q$), 136.8 (d, $^1J$(C,P) = 142.1 Hz; P*C*=), 140.8 (d, $^3J$(C,P) = 25.6 Hz; *ipso*-Ar*C*$_q$), 143.2 (d, $^3J$(C,P) = 14.0 Hz; *ipso*-Ar*C*$_q$), 149.1 (s; *p*-PAr*C*$_q$), 156.7 (dd, $^2J$(C,P) = 4.8 Hz, $^3J$(C,P) = 10.9 Hz; *o*-PAr*C*$_q$), 158.3 (s; *o*-PAr*C*$_q$), 165.3 (d, $^2J$(C,P) = 23.3 Hz; PC=*C*), 195.9 (d, $^2J$(C,P) = 8.0 Hz, $^1J$(C,W) = 125.8 Hz; *cis*-*C*O), 198.3 (d, $^2J$(C,P) = 28.2 Hz; *trans*-*C*O). IR (KBr): $\nu$ 1917 (s/br, CO$_{eq}$ and CO$_{ax}$), 2957 cm$^{-1}$ (w, CH). HR FAB-MS: calcd for $C_{36}H_{41}O_3P_2W$ (M − 2CO) 767.2040, found 767.2036. *m/z* (%): 767 (9) [M − 2CO]$^+$, 740 (3.5) [M − 3CO]$^+$, 711 (6.5) [M − 4CO]$^+$, 683 (7.5) [M − 5CO]$^+$. Anal. Found: C, 55.49; H, 5.29. Calcd for $C_{38}H_{42}O_5P_2W$: C, 55.35; H, 5.13.

**1-Phenyl-2-[2,4,6-tri-*tert*-butylphenyl]-3-diphenylmethylene-1,2-diphosphirane Pentacarbonyltungsten(0) (9b).** A solution of phosphaallene **8** (84.0 mg, 0.150 mmol) and 3-phenyl-3*H*-3-benzophosphepine complex **7b** (83.0 mg, 0.148 mmol) in toluene (6 mL) was heated at 60 °C for 30 h. Evaporation to dryness and chromatography of the residue over silica with pentane as eluent ($R_f$ = 0.24) yielded diphosphirane **9b** (64.7 mg, 50%) as a yellow solid. Crystals suitable for single-crystal X-ray structure determination were obtained from diethyl ether at +4 °C. Mp: 200 °C (dec). $^{31}$P{$^1$H} NMR (101.3 MHz, CDCl$_3$): $\delta$ −106.0 (d, $^1J$(P,P) = 77.8 Hz, *P*Mes*), −109.8 (d, $^1J$(P,P) = 77.8 Hz, $^1J$(P,W) = 256.4 Hz; *P*Ph). $^1$H NMR (250.1 MHz, CDCl$_3$): $\delta$ 1.10 (s, 9H; *p*-C(C*H*$_3$)$_3$-ArP), 1.17 (bs, 9H; *o*-C(C*H*$_3$)$_3$-ArP), 1.66 (bs, 9H; *o*-C(C*H*$_3$)$_3$-ArP), 6.66 (bs, 2H; *p*-Ar*H*), 6.94−7.00 (m, 2H; *m*-PAr*H*), 7.02−7.25 (m, 8H; Ar*H*), 7.27−7.32 (m, 2H; *m*-Ar*H*), 7.45−7.55 (m, 2H; *o*-Ar*H*), 7.90 (bs, 1H; *m*-PAr*H*). $^{13}$C{$^1$H} NMR (62.9 MHz, CDCl$_3$): $\delta$ 31.2 (s; *p*-C(*C*H$_3$)$_3$-ArP), 32.3 (bs; *o*-C(*C*H$_3$)$_3$-ArP), 33.9 (bd, $^5J$(C,P) = 11.1 Hz; *o*-C(*C*H$_3$)$_3$-ArP), 34.1 (s; *p*-*C*(CH$_3$)$_3$-ArP), 37.5 (bs; *o*-*C*(CH$_3$)$_3$-ArP), 38.7 (bs; *o*-*C*(CH$_3$)$_3$-ArP), 122.4 (bs; *p*-Ar*C*H), 127.5 (d, $^3J$(C,P) = 23.3 Hz; *m*-PPh*C*H), 128.2 (s; *m*-Ar*C*H), 128.3 (bs; *m*-PAr*C*H), 128.5 (d, $^1J$(C,P) = unresolved; *ipso*-PPh*C*H), 129.4 (d, $^4J$(C,P) = 2.7 Hz; *p*-PPh*C*H), 129.5 (s; *o*-Ar*C*H), 130.1 (s; *m*-Ar*C*H), 130.3 (s; *o*-Ar*C*H), 131.2 (bs; *m*-PAr*C*H), 133.3 (d, $^1J$(C,P) = 32.6 Hz; P*C*=), 133.6 (d, $^2J$(C,P) = 30.3 Hz; *o*-PPh*C*H), 135.1 (d, $^1J$(C,P) = 156.1 Hz; *ipso*-PAr*C*$_q$), 140.9 (d, $^3J$(C,P) = 21.0 Hz; *ipso*-Ar*C*$_q$), 141.7 (d, $^3J$(C,P) = 11.7 Hz; *ipso*-Ar*C*$_q$), 149.0 (s; *p*-PAr*C*$_q$), 156.0 (m; *o*-PAr*C*$_q$), 157.5 (s; *o*-PAr*C*$_q$), 165.1 (d, $^2J$(C,P) = 21.0 Hz; PC=*C*), 196.0 (d, $^2J$(C,P) = 7.5 Hz, $^1J$(C,W) = 126.3 Hz; *cis*-*C*O), 197.3 (d, $^2J$(C,P) = 30.2 Hz; *trans*-*C*O). IR (KBr): $\nu$ 1926 (s/br, CO$_{eq}$), 1959 (w, CO$_{eq}$), 2069 (w, CO$_{ax}$), 2961 cm$^{-1}$ (w, CH). HR FAB-MS: calcd for $C_{41}H_{43}O_3P_2W$ (M − 2CO) 829.2197, found 829.2203. *m/z* (%): 831 (6) [M −2CO]$^+$, 802 (16) [M − 3CO]$^+$, 773 (14) [M − 4CO]$^+$, 745 (38) [M − 5CO]$^+$.

**Attempted Phosphinidene Addition to Phosphaallene 8.** Procedure A: A solution of phosphaallene **8** (12.29 mg, 0.022 mmol) and 5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene pentacarbonyltungsten(0) (**6**) (10.83 mg, 0.017 mmol) was heated in toluene (0.8 mL; NMR tube) at 110 °C. After 22 h, $^{31}$P NMR spectroscopy showed that precursor **1** was fully consumed and only a small amount of product **9b** was present (17%); other products were foremost present with signals at $\delta$ 26.7 (s, 7%), 24.8 (s, 5%) 1.9 (s, 20%), −18.5 (s, 4%), −59.4 (s, 8%), −72.5 (s, 5%), and −143.8 (s, 9%). The instability of **9b** at 110 °C was also demonstrated by heating a toluene solution of the pure diphosphirane at this temperature, which led to slow decomposition without the appearance of other signals in the $^{31}$P NMR. Procedure B: A suspension of phosphaallene **7**(16.23 mg, 0.029 mmol), 5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene pentacarbonyltungsten(0) (**6**) (13.41 mg, 0.021 mmol), and CuCl (0.86 mg, 0.009 mmol) was heated in toluene (0.8 mL; NMR tube) at 55 °C. After 5.5 h, $^{31}$P NMR spectroscopy showed only unreacted phosphaallene **8** at $\delta$ 72.0 (76%) and decomposition products at $\delta$ 53.3 (s, $^1J$(P,W) = 269.6 Hz; 12%), 2.2 (s; 3%), and −83.6 to −90.5 (2%).

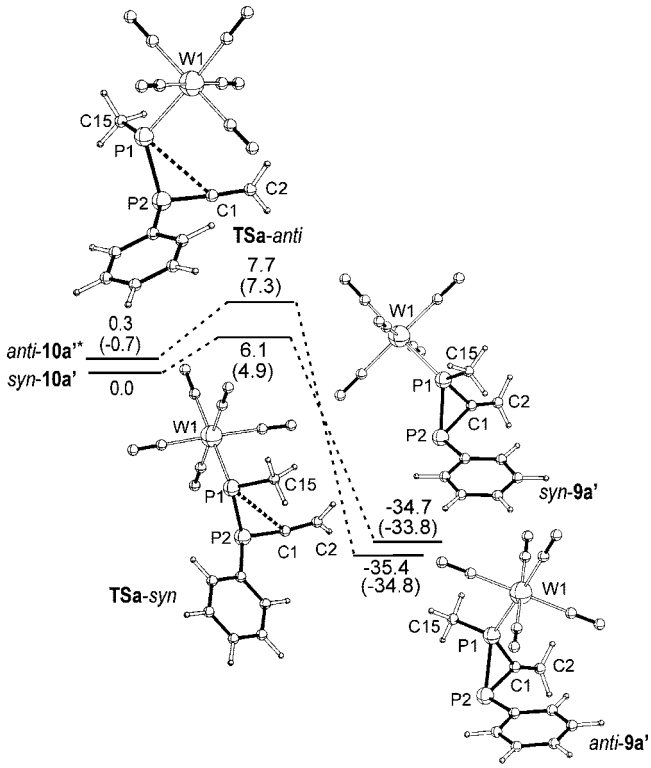


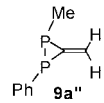
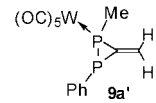
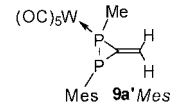

**Figure 3.** Relative B3PW91/6-31G(d) (LANL2DZ for W) energies (ZPE corrected, in kcal·mol$^{-1}$) for the rearrangement of P,P-ylides *syn*-**10a′** and *anti*-**10a′*** (enantiomer of *anti*-**10a′**) into *syn*- and *anti*-methylenediphosphiranes **9′**. The relative energies for the Ph derivatives are given in parentheses. Selected bond lengths [Å] of **TSa**-*syn*: P1−C1 3.049 (3.103), P1−P2 2.258 (2.272), P2−C1 1.667 (1.663), C1−C2 1.305 (1.304); **TSa**-*anti*: P1−C1 3.060 (3.063), P1−P2 2.279 (2.296), P2−C1 1.674 (1.673); *syn*-**9a′**: P1−P2 2.241 (2.263), P1−C1 1.801 (1.803), P2−C1 1.827 (1.827), C1−C2 1.331 (1.332); *anti*-**9a′**: P1−P2 2.241(2.255), P1−C1 1.801(1.803), P2−C1 1.827 (1.822), C1−C2 1.331 (1.332).

**X-ray Crystal Structure Determinations.** X-ray reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, $\lambda = 0.71073$ Å) up to a resolution of $(\sin \theta/\lambda)_{max} = 0.65$ Å$^{-1}$ at a temperature of 150 K. The structures were solved with automated Patterson methods[29] and refined with SHELXL-97[30] against $F^2$ of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[31]

Crystal structure determination of compound **9a**: $C_{38}H_{42}O_5P_2W$, fw = 824.51, yellow block, 0.34 × 0.18 × 0.15 mm$^3$, monoclinic, $P2_1/c$ (no. 14), $a$ = 11.5587(1) Å, $b$ = 24.3230(2) Å, $c$ = 15.4742(1) Å, $\beta$ = 119.9126(3)°, $V$ = 3770.91(5) Å$^3$, $Z$ = 4, $D_x$ = 1.452 g/cm$^3$, $\mu$ = 3.187 mm$^{-1}$; 75 860 reflections were measured. An absorption correction based on multiple measured reflections was applied (0.31−0.62 correction range); 8621 reflections were unique ($R_{int}$ = 0.042); 425 parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0220/0.0458. R1/wR2 [all reflns]: 0.0289/0.0479. $S$ = 1.073. Residual electron density between −0.78 and 1.01 e/Å$^3$.

Crystal structure determination of compound **9b**: $C_{43}H_{44}O_5P_2W$, fw = 886.57, yellow block, 0.39 × 0.24 × 0.21 mm$^3$, triclinic, $P\bar{1}$ (no. 2), $a$ = 11.3216(4) Å, $b$ = 13.2755(4) Å, $c$ = 14.5331(3) Å, $\alpha$ = 70.009(1)°, $\beta$ = 78.960(2)°, $\gamma$ = 75.101(1)°, $V$ = 1970.74(10) Å$^3$, $Z$ = 2, $D_x$ = 1.494 g/cm$^3$, $\mu$ = 3.055 mm$^{-1}$; 53 642 reflections were measured. An absorption correction based on multiple measured reflections was applied (0.24−0.52 correction range); 8957 reflections were unique ($R_{int}$ = 0.022); 469 parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0149/0.0317. R1/wR2 [all reflns]: 0.0181/0.0324. $S$ = 1.092. Residual electron density between −0.47 and 0.39 e/Å$^3$.

**Table 1. Relative B3PW91/6-31G(d) (LANL2DZ for W) Energies (ZPE corrected, in kcal·mol$^{-1}$) of Model Systems 9a′ and 9a″ (without W(CO)$_5$) and 9a′*Mes* (mesityl instead of Ph on the uncomplexed P)**

| |  **9a″** |  **9a′** |  **9a′***Mes* |
|---|---|---|---|
| *syn*-**10a′** | 0.0 | 0.0 | 0.0 |
| **TSa**-*syn* | 11.7 | 6.1 | 7.9 |
| *syn*-**9a′** | –36.4 | –34.7 | –32.8 |
| *anti*-**10a′** | 1.8 | 0.3 | –0.6 |
| **TSa**-*anti* | 9.1 | 7.7 | 10.0 |
| *anti*-**9a′** | –38.5 | –35.4 | –32.4 |

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**Supporting Information Available:** Cartesian coordinates (Å) and energies (au) of all stationary points. Cif files with crystallographic data and copies of the NMR spectra of compounds **9a** and **9b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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