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Revisiting the Phospha-Wittig–Horner Reaction

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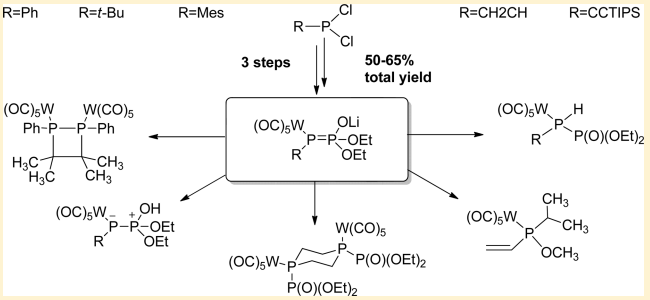
Supporting Information

ABSTRACT: *P,P*-Dichlorophosphines **2a–c** ($RPCl_2$, R = Ph (**a**), *t*-Bu (**b**), 2,4,6-Me_3Ph (**c**)) and *P,P*-dibromophosphines **4d,e** ($RPBr_2$, R = $(i\text{-Pr})_3SiC{\equiv}C$ (**d**) and $H_2C{=}CH$ (**e**)) react with triethylphosphite under Michaelis–Arbuzov conditions to give phosphinodiphosphonates **3a–e** in quantitative yields. After complexation to $W(CO)_5$ and treatment with CH_3ONa, phospha-Wittig–Horner reagents **9a,b** are obtained on a multigram scale in good overall yield. Phospha-Wittig–Horner reagents with unsaturated substituents at ^{III}P (**10d,e**) can be prepared in analogous procedures; however, they prevail in an unusual ylide form that allows conjugation between the lone pair and the acetylene and vinyl π-systems, respectively. Phosphinophosphonate **9a** has been characterized by X-ray crystallography and is shown to react smoothly with acetone within minutes. The resulting $W(CO)_5$-coordinated phosphaalkene is shown to dimerize to a 1,2-diphosphitane or to undergo a 1,3-proton shift depending on the reaction conditions. In addition, a one-pot synthetic sequence starting from $W(CO)_5$-coordinated phosphinodiphosphonates **5d,e** has been developed to engage compounds with vinyl and acetylene substituents in phospha-Wittig–Horner reactions.



INTRODUCTION

The direct conversion of aldehydes and ketones into olefins using phosphonium ylide reagents is an important reaction in organic chemistry and was awarded the Nobel Prize in chemistry to Georg Wittig in 1979.[1] Inspired by the similarities between low-valent phosphorus and carbon chemistry,[2,3] Mathey and co-workers developed the so-called phospha-Wittig reactions, i.e., an analogous procedure that allows the access of phosphaalkenes from carbonyl compounds (Scheme 1).[4,5] In analogy to the carbon case, two different reagents have been reported that can be used for these transformations. Both consist of a tervalent phosphorus center (P^{III}) that is bound to a high-valent P^V unit. Reagents that contain a $-PR_3$ group as the P^V unit (R = Me, Bu, Ph, etc.) have been termed phospha-Wittig reagents (type A, Scheme 1), while those that contain $(RO)_2P{=}O$ units are usually referred to as phospha-Wittig–Horner reagents (type B, Scheme 1).

Preparation of both type of reagents is greatly facilitated by the coordination of a metal–carbonyl fragment, frequently a $W(CO)_5$ unit, to stabilize the highly reactive low-valent phosphorus center. Depending on the structure of the P^V center, two different reactivity patterns can be observed: reagents of type A can be easily prepared in only two steps starting from dichlorophosphines, but are reactive only toward aldehydes.[6,7] On the other hand, $W(CO)_5$-coordinated phosphinophosphonates (type B) have been shown to react with aldehydes *and* ketones under basic conditions to afford $W(CO)_5$-coordinated phosphaalkenes.[4,5] The latter reaction produces phosphaalkenes that are more stable than those that are accessible from aldehydes due to the presence of two substituents at the P=C carbon that kinetically stabilize the P=C bond. In a further development of the above protocols, Protasiewicz and co-workers developed a metal-free "one-pot" protocol for the preparation of phosphanylidenephosphoranes (type A), reported its crystal structure,[8] and demonstrated their reactivity toward aldehydes.[9] However it should be noted that this protocol is applicable mainly for *P,P*-dichlorophosphines bearing bulky substituents (Mes* or Dmp), while smaller substituents give unsatisfactory results.[6] For reagents of type B, a metal-free version has remained elusive.

We have recently commenced a program to combine low-valent phosphorus with acetylene chemistry, thus introducing intrinsic metal binding sites into oligoacetylene scaffolds.[10−12] At the same time, *P*-inclusion in the resulting acetylenic phosphaalkenes leads to decreased HOMO–LUMO gaps compared to those in all-carbon-based compounds with comparable π-systems.[13−16] In this context, we became interested in the phospha-Wittig–Horner reaction, as it appears as an elegant entry into hitherto unavailable *P,C*-diacetylenic phosphaalkenes. Since the latter compounds presumably suffer from stability issues, $W(CO)_5$ coordination is desirable to stabilize the P=C bond.[17]

During first exploratory studies, severe difficulties in the preparation of reported phospha-Wittig–Horner reagents were encountered that prompted us to develop an alternative approach that allows the preparation of the reagents on a multigram scale. With certain adjustments, the reaction sequence is feasible also for substrates with nontraditional unsaturated *P*-substituents. Depending on the substituent at

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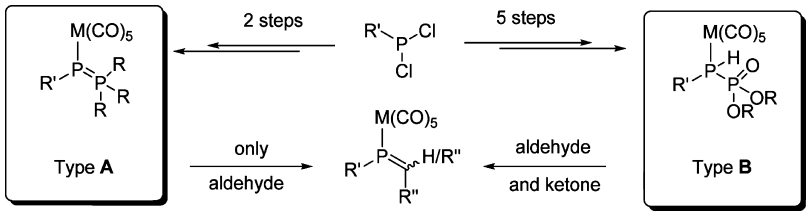
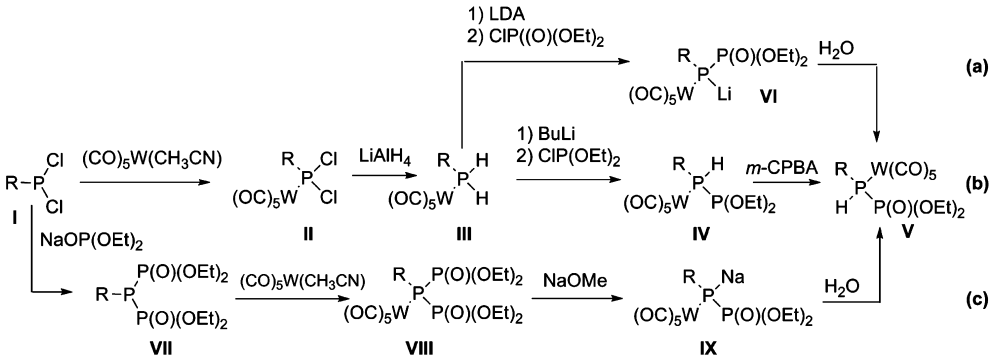
Scheme 1. Difference in Reactivity of Phospha-Wittig (Type A) and Phospha-Wittig–Horner (Type B) Reagents



Scheme 2. Summary of Literature Procedures toward Phospha–Wittig Reagents[a]



[a]Conditions: (a) R = Ph, *t*-Bu,[5] (b) R = Mes, Ment,[18,19] (c) R = Me, Ph, *t*-Bu, PhCH=CH, BuOCH=CH, 2-thienyl.[18].

P^{III}, different isomeric forms of the phospha-Wittig–Horner reagents are observed.

RESULTS AND DISCUSSION

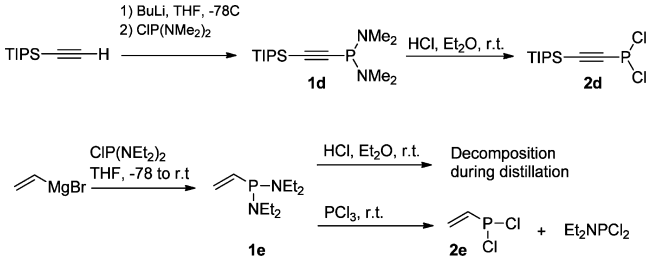
Scheme 2 summarizes three synthetic protocols that are described in the literature for the preparation of phospha-Wittig–Horner reagents.[4,5,18,19]

The crucial step of routes (a) and (b) in Scheme 2 involves 2-fold lithiation of the primary phosphine tungsten complex **III**, which in our hands proved to be difficult. According to ^{31}P NMR analysis of the reaction mixture, **III** undergoes only partial lithiation with BuLi or *t*-BuLi and only at temperatures higher than −20°, irrespective of whether commercial or freshly prepared BuLi was used. Warming the mixture to higher temperatures leads to decomposition. Lithiation was alternatively attempted with LDA, an approach that initially converts primary phosphine **III** to its monolithium salt; however, it ultimately suffers from the addition of $[(i\text{-Pr})_2N]^-$ to the phosphorus precursor and the formation of *N*,*N*-diisopropylamino-*O*,*O*-diethylphosphonate, which is difficult to separate from the desired product by chromatography. Protocol (c) is the synthetically most reliable; however, it requires the preparation of the $NaOP(OEt)_2$ reagent. The latter is somewhat tedious, as the amount of added sodium has to be controlled precisely, as an excess will reduce the dichlorophosphine **I**. In our hands, all three routes (a)–(c) unfortunately produce numerous side products that are difficult, if not impossible, to remove by recrystallization and column chromatography.

Considering the above problems, we sought an alternative access to phospha-Wittig–Horner reagents that would circumvent some of the problems encountered in the published procedures. In particular the Michaelis–Arbuzov reaction seemed to be a viable alternative to convert *P*,*P*-dichlorophosphines to the phosphinodiphosphonates **VIII**.[20] With our interest in phosphaalkenes that are in π-conjugation with other unsaturated organic groups, phospha-Wittig–Horner reagents with unprecedented terminal vinyl and TIPS-acetylene (TIPS = triisopropylsilyl) substituents were prepared in addition to those that carry more conventional Ph, *t*-Bu, and Mes (Mes = $2,4,6\text{-Me}_3\text{Ph}$) groups.

Preparation of *P*,*P*-Dichlorophosphine. While $PhPCl_2$ (**2a**) and *t*-$BuPCl_2$ (**2b**) are commercially available, $MesPCl_2$ (**2c**) and $TIPSCCPCl_2$ (**2d**) can be prepared by literature methods,[21] the latter in analogy with a procedure for the synthesis of $PhCCPCl_2$.[22] The literature procedure for the preparation of $H_2CCHPCl_2$ (**2e**) however requires the use of highly toxic divinyl mercury,[23] and it is therefore imperative to develop a new synthetic protocol for **2e** (Scheme 3).

Scheme 3. Preparation of $RPCl_2$ 2d,e



Vinyl magnesium bromide was thus reacted with bis(diethylamino)chlorophosphine to afford bis(diethylamino)vinylphosphine **1e** in good yield. Conversion to the corresponding dichlorophosphine **2e** using an ethereal solution of anhydrous hydrochloric acid results in reaction mixtures that are difficult to purify due to considerable heat, oxygen, and moisture sensitivity of **2e**. To avoid complicated purification steps, we developed an alternative procedure that is based on a chloride/amine exchange between bis(diethylamino)vinylphosphine **1e** and phosphorus trichloride. Treatment of bis(diethylamino)vinylphosphine **1e** with two equivalents of PCl_3 under solvent-free conditions at room temperature results

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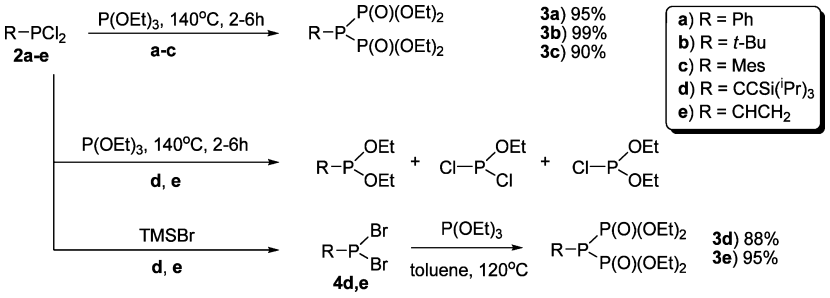
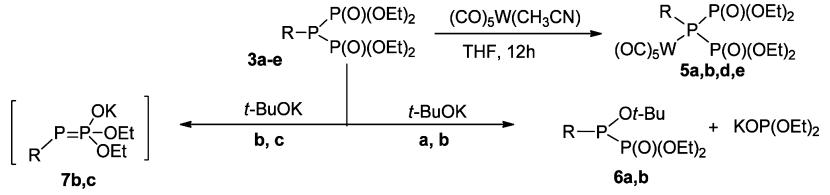
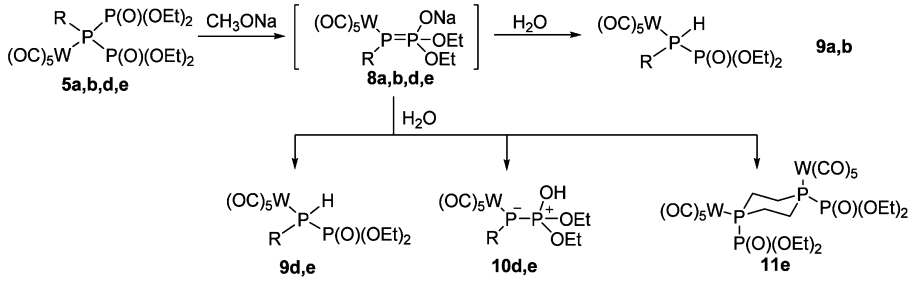
Scheme 4. Michaelis–Arbuzov Reaction of $RPCl_2$ 2a–e to Phosphinodiphosphonates 3a–e



Scheme 5. Coordination of $W(CO)_5$ to 3a–e and Treatment of the Latter with Potassium *tert*-Butoxide



Scheme 6. Hydrolysis of Phosphinodiphosphonates Metal Complexes



in quantitative formation of desired *P,P*-dichlorovinylphosphine **2e** and dichloro(diethylamino)phosphine within 5 minutes. **2e** is isolated as a colorless liquid in 75% yield by vacuum distillation at −20 °C.

Michaelis–Arbuzov Phosphorylation of *P,P*-Dichlorophosphines. With **2a–e** in hand, their reactivity with triethylphosphite in Michaelis–Arbuzov reactions to afford phosphinodiphosphonates **3a–e** was investigated (Scheme 4).

While in the case of **2a–c**, the desired phosphinodiphosphonates **3a–c** could be obtained in good yields, the reaction of **2d,e** proceeded very dissatisfactory, and only minor amounts of **3d,e** could be isolated. ^{31}P NMR spectra of the reaction mixtures suggest that the majority of **2d,e** undergoes scrambling reactions with triethylphosphite to afford mixtures of ethylchlorophosphites with varying numbers of chloro and ethoxy groups (Scheme 4). Since bromides are known to be more reactive than chlorides and react under milder conditions in Michaelis–Arbuzov reactions,[24] we converted **2d,e** into the corresponding *P,P*-dibromophosphines **4d,e**. This transformation is achieved using trimethylsilyl bromide as bromide source under solvent-free conditions.[25] Conversion is complete after 15 min at room temperature, and the dibromides **4d,e** are obtained in good yields (88–92%). With the dibromides in hand, their reaction with $P(OEt)_3$ proceeds smoothly and affords phosphinodiphosphonates **3d,e** as colorless, oxygen- and water-sensitive liquids in good yield.

Coordination to $W(CO)_5$ Core. At the stage of phosphinodiphosphonates **3a–e**, $W(CO)_5$ metal fragments were introduced to increase the stability of the subsequent phospha-Wittig–Horner reagents and their phosphaalkenes. Thus, freshly prepared $W(CO)_5CH_3CN$[5] was mixed with solutions of compounds **3a–e** in THF to afford complexes **5a,b,d,e** in moderate to good yields (65–84%). Only in the case of mesityl-substituted **3c** could no coordination to the metal fragment be observed due to steric crowding, even after prolonged heating at increased temperatures.

Complexes **5** are moderately moisture sensitive, oily compounds that can be stored for several weeks at −20 °C under an argon atmosphere without visible decomposition. While phospha-Wittig reagents of type A that lack a stabilizing metal center are known,[9] the corresponding phospha-Wittig–Horner reagents of type B have previously been reported only as metal complexes. With **3a–c** in hand, we examined the possibility to prepare such species by hydrolysis. The difficulties to do so became immediately evident when **2a** was treated with potassium *tert*-butoxide, resulting in the replacement of one phosphonate group by a *tert*-butoxide and the formation of **6a** and $KOP(OEt)_2$. In the case of **3b**, a new product (**7b**) was observed in addition to the formation of the analogous **6b**. A corresponding new species (**7c**) featured as the exclusive product in the reaction of the mesityl-substituted **3c** and was identified as the enolate form of the phospha-Wittig–Horner reagent of type B (Scheme 5). The assignment can be made on the basis of the characteristic high-field ^{31}P NMR chemical shift of the P^{III} center ($\delta(P^{III})$ = −165.6 ppm, $\delta(P^{V})$ = 79.8 ppm) and the unusually large $^1J_{P=P}$ = 569 Hz coupling constant.[26] **7b,c** can be generated only *in situ*, and attempts to quench and isolate the salts resulted in decomposition. Nevertheless, our

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experiments suggest that a certain amount of steric bulkiness will prevent reaction at the tervalent phosphorus center and can drive the reaction toward **7**.

Also for the metal-coordinated **5a,b,d,e**, treatment with NaOMe or KO*t*-Bu results in the first instance in the formation of the enolate form of the phospha-Wittig–Horner reagents **8a,b,d,e** (Scheme 6) with characteristic ^{31}P NMR spectra that feature two doublets typically around 65 ppm (P^V) and between −113.4 (**8e**) and −75.4 (**8b**) ppm (P^{III}) with large $^1J_{P-P}$ coupling constants between 340 (**8e**) and 429.7 (**8b**) Hz.

Aqueous workup of **8a,b** that possess somewhat classical substituents at the P^{III} center proceeds without difficulties, and **9a,b** can be obtained in good yield. In fact, **9a** could be obtained from **2a** on a 15 g scale with a total yield of 62% over three steps. In our hands, the new procedure that relies on a Michaelis–Arbuzov reaction is a vast improvement compared to existing literature methods (Scheme 2). Compound **9a** needs to be stored at low temperature under inert atmosphere to avoid decomposition, which otherwise occurs within several hours at room temperature. Recrystallization from pentane at −30 °C gives **9a** as white crystals suitable for X-ray analysis. Figure 1 shows the first crystal structure of a phospha-Wittig–Horner reagent. The crystallographic cell of complex **9a** consists of two molecules that interact with each other via a hydrogen bond (D–H···A = 2.676 Å and dihedral angle D–H···A = 168.7°) between the phosphine proton of the first and a phosphonate oxygen of the second molecule. The tendency to form hydrogen bonds is consistent with the necessity to use hydrophobic silica gel for purification of the compound. The P–W distance is 2.49 Å and, thus, in the expected region for compounds of the general formula $(CO)_5$W-PR_3.[27] Complex **9a** adopts a staggered conformation across the P–P bond in the solid state. The bulky $W(CO)_5$ fragment avoids steric congestion with the ethoxy groups by having a −sc relationship with the P=O according to the Klyne–Prelog classification. The W–P–P=O dihedral angles in the two molecules of the crystallographic cell are 57.0(2)° for W1–P1–P2–O6 and 49.4(2)° for W2–P3–P4–O21.

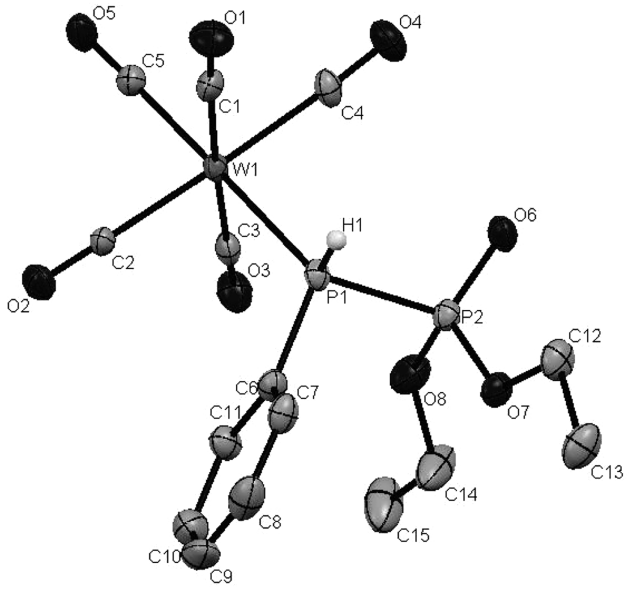
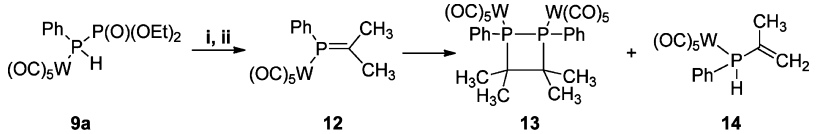


Figure 1. Crystal structure of phospha-Wittig–Horner complex **9a**. ORTEP drawing (50% probability) All hydrogens except for H1 are omitted for clarity. Selected bond lengths (Å): W1–P1 2.4966(16), P1–H1 1.000, P1–P2 2.187(2), P2=O6 1.471(5), P2–O7 1.575(5), P2–O8 1.565(5).

While **9a,b** can be obtained in high yields, a more complicated picture emerges during the quenching of **8d,e** containing appended π-systems (Scheme 6). In the case of TIPS-ethynyl-substituted **8d**, treatment with aqueous NH_4Cl results in the formation of **10d**, which can in principle be described by two structures: as the enol form of the desired phospha-Wittig–Horner reagent with a formal P=P double bond or as an ylide as depicted in Scheme 6. The structural assignment of the product was made on the basis of the rather small coupling constant of $^1J_{P-P}$ = 89 Hz, which points toward an ylide-type structure. The stability of this compound as compared to the elusive phospha-Wittig–Horner reagent **9d** is presumably due to π-conjugation of the lone pair at the low-valent phosphorus center to the appended acetylene unit. The conjugation is also evident from the UV/vis spectrum of **10d** (in CH_3OH), which features a longest wavelength absorption maximum as a shoulder around 360 nm that trails well into the visible. The corresponding absorption of phenyl-substituted **9a** can be observed at higher energy around 345 nm. The quenching products of **8e** resemble those of **8d**, even though an additional complication obscures the picture somewhat. When **8e** is quenched with aqueous NH_4Cl, **10e** is observed only in minor amounts, and a new major product (**11e**) is detected instead. **11e** is the dimerization product of a reaction where a ^{III}P nucleophile has attacked the vinyl group of a second compound, followed by an intramolecular ring-closure following the same mechanism. It is noteworthy that only the *cis*-isomer is formed, the structure of which can easily be assigned by ^{31}P and ^{13}C NMR.[28] Similar reactivity was observed by Mathey et al. with the divinylphosphine(pentacarbonyl) tungsten complex, which upon treatment with BuLi forms 1,4-diphosphorinane.[29] The dimerization can however be avoided by quenching **8e** under strongly acidic conditions, thereby preventing the formation of presumably anionic P^{III} nucleophiles. Addition of an aqueous solution of *p*-toluene sulfonic acid results in the initial formation of **9e**, which however isomerizes to the thermodynamically more stable **10e** over hours. Phosphinylidenephosphites **10d,e** are stable compounds and can be purified by column chromatography.

Scheme 7. Phospha-Wittig–Horner Reaction of 9a with Acetone to Form Phosphaalkene 12 and Subsequent Head-to-Head Dimerization and 1,3-Proton Shift[a]



9a **12** **13** **14**

[a]Conditions: (i) LDA, THF, −78 °C, 30 min, or DABCO, rt; (ii) dry acetone, rt, 6–12 h.

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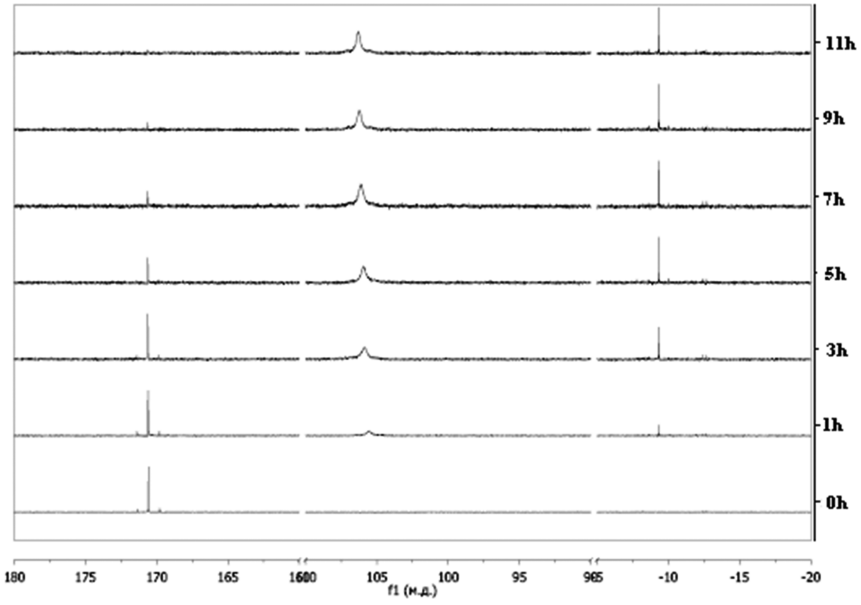
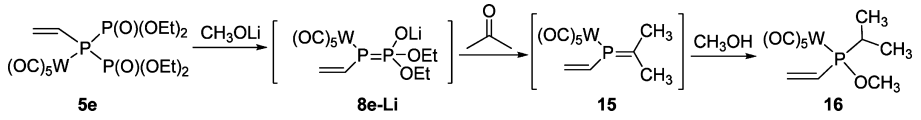


Figure 2. ^{31}P NMR spectroscopic study of the transformation of **12** to **13** in THF solution, using C_6D_6 as internal standard. ^{31}P NMR after 5 min, 1 h, 3 h, 5 h, 7 h, 9 h, and 11 h. Reaction was run at 22 °C, using 20 mg (0.035 mmol) of **9a** in 0.5 mL of THF and 4 mg (0.035 mmol) of DABCO.

Scheme 8. *In Situ* Generation of 8e-Li and Its Reaction with Acetone



5e 8e-Li 15 16

Test Reaction with Acetone. In order to verify the reactivity of the phospha-Wittig–Horner reagents and to investigate the effect of the different substituents and isomeric forms on the formation of phosphaalkenes, test reactions of **9a,e** with acetone were performed. Addition of DABCO to **9a** initiates the experiment (Scheme 7), the course of which was monitored by ^{31}P{H} NMR. As visible from Figure 2, the reaction is rather fast and phosphaalkene **12** can be identified by its ^{31}P chemical shift at δ_{THF} = 170 ppm (δ_{CDCl3} = 176 ppm)[4] as the only product after 5 minutes (Scheme 5). Upon prolonging the reaction times, phosphaalkene **12** is consumed and the new species **13** emerges, which is characterized by a ^{31}P chemical shift of δ = 105 ppm. The conversion is complete after ca. 10 hours. HRMS studies show a molecular weight of m/z = 1092.89844 (**13** + $2H_2O$ + Ag) for the new species, i.e., twice that of phosphaalkene **12**. Compound **13** shows a characteristic ABX coupling pattern of diasteriotopic methyl groups to two phosphorus atoms in the ^{1}H NMR. Together, the analytical data allow the assignment of a 1,2-diphosphitane structure to complex **13**. Head-to-head type dimerization of **12** can be explained by steric factors as the longer P–P bond compared to the C–P bond presumably allows the bulky $W(CO)_5$ groups to avoid severe steric repulsion.

The head-to-head dimerization that we observe for **12** contrasts a report by Marinetti et al., who describe a different subsequent chemistry for **12**.[5] According to this report, a 1,3-proton shift occurs on **12** and a secondary vinylphosphane, **14**, is obtained instead. In our hands, the 1,3-proton shift is observed only as a side reactions in less than 3% yield, as judged by ^{31}P NMR. The discrepancy between the two experimental findings lies in the amount of DABCO that is used to promote the reaction. Increasing the amount of base to two equivalents shifts the product distribution of **13** vs **14** to 1:1. It is necessary to underline that under such reaction conditions the ^{31}P NMR signal of **13** is very broad and relatively easy to overlook.

The reaction between **9a** and acetone can also be promoted by the addition of one equivalent of LDA. The transient lithium salt that is formed quantitatively after 30 minutes at −30 °C is best described as the lithium analogue of **8a** with P═P double-bond character and ^{31}P NMR chemical shifts of 62.7 and −107.5 ppm ($^1J_{P=P}$ = 383.3 Hz).[5] Addition of acetone and stirring of the reaction mixture at room temperature results in mixtures of **12** and **13**, the ratio of which depends on reaction times.

The presence of unsaturated substituents at the P^{III} disallows the DABCO-promoted preparation of phosphaalkenes from **9d,e**. However, a one-pot synthetic strategy that generates the Li analogue of **8e** (^{31}P NMR: 63.4 (P^V) and −113.2 (P^{III}) with $^1J_{P=P}$ = 350 Hz) *in situ* starting from bis(phosphonato)-phosphine **5e** upon treatment with methanolic lithium methoxide can be used for the reaction with ketones such as acetone. After 8 hours, **8e-Li** is completely converted to phosphaalkene **15**, which can be trapped by the addition of methanol (Scheme 8). Phosphaalkene **15** is thermally unstable and decomposes in the absence of trapping reagent, presumably to polymeric materials.

■ CONCLUSIONS

We have developed a reliable synthetic protocol that allows the preparation of phospha-Wittig–Horner reagents on a multi-gram scale in three steps and good overall yields. Compound **9a** is the first phospha-Wittig–Horner reagent that has structurally been characterized and has been shown to react quantitatively with acetone to give phosphaalkene **12** in less than 5 minutes.

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Prolonged reaction times result in subsequent transformations to 1,2-diphosphitane **13** and vinylphosphine **14**. Nontraditional phospha-Wittig–Horner reagents with unsaturated, π-conjugated substituents at P^{III} can be prepared in analogous procedures; however, they prevail in an unusual ylide form. A one-pot synthetic sequence starting from phosphinodiphosphonates **5** has been developed to engage also the compounds with such unsaturated substituents in phospha-Wittig–Horner reactions. The knowledge obtained in this work encourages the use of phospha-Wittig–Horner reagents as starting materials for the construction of highly unsaturated P,C systems. Efforts in these directions are currently in progress in our laboratories.

EXPERIMENTAL SECTION

General Procedures. All reactions were performed under argon using Schlenck techniques. Diethyl ether and THF were freshly distilled from sodium/benzophenone prior to use. ^{1}H, ^{13}C, and ^{31}P spectra were recorded on a 400 MHz spectrometer. Chemical shifts (ppm) were reported and referenced to the internal signal of residual protic solvent. High-resolution mass spectral analyses (HRMS) were performed on a high-resolution and FTMS+pNSI mass spectrometer (OrbitrapXL) or on a MicroTOF spectrometer with ESI source.

X-ray Data. Crystal structure data for compound **9a** were deposited at the Cambridge Crystallographic Data Centre under the number CCDC 816416.

Bis((*N*,*N*-dimethyl)amino)TIPS-acetylenephosphine (1d). A solution of 7.53 g (0.041 mol) of TIPS-acetylene in 250 mL of THF was cooled to −78 °C, and 16.4 mL (2.5 M solution in THF) of BuLi was added dropwise over 20 min. The reaction mixture was stirred for 30 min at −78 °C and 10 min at room temperature. The reaction mixture was then cooled to −40 °C, and a solution of 6.38 g (0.041 mol) of ((*N*,*N*-dimethyl)diamino)chlorophosphine in 10 mL of THF was added over 10 min. The reaction mixture was allowed to warm to room temperature and stirred for an additional 4 h. The solution was concentrated under vacuum to a volume of 50 mL. The residue was diluted with dry pentane (100 mL), the formed precipitate removed by filtration, and the solvent removed by vacuum. The remaining oily residue was fractionally distilled under vacuum (bp 176 °C/1 Torr), affording product as a colorless oil. Yield: 10 g, 81%. ^{31}P ($CDCl_3$), {H}): 69.8. ^{1}H ($CDCl_3$): 2.74 (d, $^3J_{H-P}$ = 12.0, 12H, NCH_3), 1.09 (s, 21H, $Si(CH(CH_3)_2)_3$). ^{13}C ($CDCl_3$, {H}): 108.7 (d, $^1J_{C-P}$ = 2.0, −C≡C−P), 106.8 (d, $^2J_{C-P}$ = 5.0, −C≡C−P), 41.1 (d, $^2J_{C-P}$ = 15.1, NCH_3), 18.6 (s, $Si(CH(\underline{C}H_3)_2)_3$), 11.2 (s, $Si(\underline{C}H(CH_3)_2)_3$). HRMS (methanol): found 317.2171, calcd 317.2178, $C_{15}H_{34}N_2PSi$, $[mol + H]^+$.

Bis((*N*,*N*-diethyl)amino)vinylphosphine (1e). A solution of 21.07 g (0.1 mol) of bis((*N*,*N*-diethyl)amino)chlorophosphine in 250 mL of THF was cooled to −78 °C, and 100 mL of a solution of vinylmagnesium bromide (1 M solution in THF) was added over 30 min. The resulting suspension was allowed to warm to room temperature and stirred for 12 h. The solvent was removed under vacuum until ca. 100 mL of a suspension was left. Then 150 mL of dry pentane was added to the suspension, the solid removed by filtration, and the filtrate concentrated under vacuum. The resulting yellowish oil was fractionally distilled to afford **1e** as a colorless oil. Yield: 15.4 g, 76%. ^{31}P ($CDCl_3$, {H}): 90.0. ^{1}H ($CDCl_3$): 6.16 (ddd, $^2J_{C-P}$ = 24.2, $^3J_{H-H}$ = 18.5, $^3J_{H-H}$ = 12.2, 1H, $PC\underline{H}CH_2$), 5.66 (ddd, $^3J_{H-P}$ = 20.6, $^3J_{H-H}$ = 12.2, $^2J_{H-H}$ = 2.6, 1H, $PCHC\underline{H}_2$), 5.46 (ddd, $^3J_{H-H}$ = 18.5, $^3J_{H-P}$ = 8.1, $^2J_{H-H}$ = 2.6, $PCHC\underline{H}_2$), 3.10–2.94 (m, 8H, $NC\underline{H}_2CH_3$), 1.03 (t, $^3J_{H-H}$ = 7.1, 12H, $NCH_2C\underline{H}_3$). ^{13}C ($CDCl_3$, {H}): 139.8 (d, $^1J_{C-P}$ = 1.5, $P\underline{C}HCH_2$), 124.1 (d, $^2J_{C-P}$ = 15.8, $PCH\underline{C}H_2$), 42.7 (d, $^2J_{C-P}$ = 15.4, $N\underline{C}H_2CH_3$), 14.8 (d, $^3J_{C-P}$ = 3.5, $NCH_2\underline{C}H_3$).

***P*,*P*-Dichloro(TIPS-acetylene)phosphine (2d).** A solution of 5 g (0.017 mol) of bis((*N*,*N*-dimethyl)amino)TIPS-acetylenephosphine (**1d**) in 250 mL of diethyl ether was cooled to −30 °C, and 33.3 mL (2 M solution in diethyl ether) of hydrochloric acid solution was added dropwise over 15 min. A white precipitate formed immediately. The suspension was allowed to warm to room temperature and stirred for 12 h. The solid was removed by filtration under argon, and the filtrate concentrated under vacuum to afford a pale yellow oil. Fractional distillation gives *P*,*P*-dichloro(TIPS-acetylene)phosphine (**2d**) as a colorless, water- and oxygen-sensitive oil (bp 170 °C/1 Torr). Yield: 3.01 g, 63%. ^{31}P ($CDCl_3$), {H}): 117. ^{1}H ($CDCl_3$): 1.11 (s, 21H, $Si(CH(CH_3)_2)_3$). ^{13}C ($CDCl_3$, {H}): 122.1 (d, $^2J_{C-P}$ = 1.0, −C≡C−P), 105.7 (d, $^1J_{C-P}$ = 81, −C≡C−P), 18.4 (s, $Si(CH(CH_3)_2)_3$), 11.0 (d, $^5J_{C-P}$ = 2.0, $Si(\underline{C}H(CH_3)_2)_3$).

***P*,*P*-Dichlorovinylphosphine (2e).** A 1.8 g (8.9 mmol) of **1e** was placed in a flame-dried flask connected to a Schlenck tube, and 2.44 g (17.8 mmol) of phosphorus trichloride was added in one portion. The reaction mixture was stirred for 15 min at rt. After this, the Schlenck tube was cooled to −78 °C and exposed to vacuum (12 Torr). **2e** was collected in a Schlenck flask as a very moisture- and oxygen-sensitive and highly odorous, colorless liquid. Yield: 0.7 g, 61%. ^{31}P ($CDCl_3$, {H}): 159.7. ^{1}H ($CDCl_3$): 6.9 (ddd, $^3J_{H-H}$ = 18.7, $^2J_{H-P}$ = 12.6, $^3J_{H-H}$ = 11.9, $PC\underline{H}CH_2$), 6.10 (dd, $^3J_{H-H}$ = 18.7, $^3J_{H-P}$ = 18.7, $PCHC\underline{H}_2$), 6.06 (dd, $^3J_{H-P}$ = 45.18, $^3J_{H-H}$ = 11.9, $PCHC\underline{H}_2$). ^{13}C ($CDCl_3$, {H}): 142.2 (d, $^1J_{C-P}$ = 51.3, $P\underline{C}HCH_2$), 130.6 (d, $^2J_{C-P}$ = 46.2, $PCH\underline{C}H_2$).

Michaelis–Arbuzov Reaction of 1a–c with Triethylphosphite. *Bis(O,O-diethyl)phosphonato)-phenylphosphine (3a).* A 14.69 g (0.088 mol) of *O*,*O*,*O*-triethylphosphite was added dropwise to a solution of 7.91 g (0.044 mol) of *P*,*P*-dichlorophenylphosphine **2a** in 25 mL of dry toluene at room temperature. The reaction mixture was slowly heated to 110 °C (gas evolution starts at ca. 60 °C) and heated to reflux for 6 h. After complete conversion of the starting materials (as judged by ^{31}P NMR analysis), the reaction mixture was cooled to room temperature. Removal of all volatiles under vacuum gave **3a** as a colorless oil. The compound was pure by ^{1}H NMR analysis and was used in the next step without further purification. NMR data are consistent with those described in the literature.[20] Yield: 95%. ^{31}P ($CDCl_3$, {H}): 28.5 (d, P^V), −62.0 (t, $^1J_{P-P}$= 131.8, P^{III}).

Bis(O,O-diethyl)phosphonato)tert-butylphosphine (3b). A 3.21 g (0.02 mol) of **2b** was placed in a flame-dried flask, and 6.71 g (0.04 mol) of *O*,*O*,*O*-triethylphosphite was added dropwise at room temperature. The reaction mixture was slowly heated to 140 °C (gas evolution starts at ca. 110 °C) and heated for 6 h. After complete conversion of the starting materials (as judged by ^{31}P NMR analysis), the reaction mixture was cooled to room temperature. Removal of all volatiles under vacuum gave a colorless oil of **3b** as a pure compound by ^{1}H NMR analysis, which was used in the next step without further purification. NMR data are consistent with those described in the literature.[18] Yield: 99%. ^{31}P ($CDCl_3$, {H}): 31.3 (d, $^1J_{P-P}$ = 210.4, P^V), −33.3 (t, P^{III}). ^{1}H ($CDCl_3$): 4.19–4.11 (m, 8H, $OC\underline{H}_2CH_3$), 1.37 (d, $^3J_{H-P}$ = 12.0, 9H, *t*-Bu), 1.28 (t, $^3J_{H-H}$ = 8, 6H, $OCH_2C\underline{H}_3$), 1.27 (t, $^3J_{H-H}$ = 8, 6H, $OCH_2C\underline{H}_3$).

Bis(O,O-diethyl)phosphonato)mesitylphosphine (3c). **3c** was prepared applying the same protocol as for **3b** using 2.27 g (10.3 mmol) of **2c** and 3.4 g (21 mmol) of *O*,*O*,*O*-triethylphosphite. Reaction mixture was heated for 2 h at 140 °C. Resulting crude **3c** was dissolved in diethyl ether and chromatographed on silica gel using diethyl ether to elute side products and methanol to elute **3c** as a colorless oil. Yield: 4 g, 90%. ^{31}P ($CDCl_3$, {H}): 29.4 (d, $^1J_{P-P}$ = 187.7, P^V), −73.2 (t, P^{III}). ^{1}H ($CDCl_3$): 6.91 (s, 2H, Ph), 4.24–4.09 (bs, 8H, $OC\underline{H}_2CH_3$), 2.75–2.60 (bs, 6H, *o*-$C\underline{H}_3$Ph), 3.33 (s, 3H, *p*-$C\underline{H}_3$Ph), 1.27 (bs, 12H, $OCH_2C\underline{H}_3$). ^{13}C ($CDCl_3$, {H}): 146.5 (s, *o*-Ph), 141.1 (s, *p*-Ph), 129.8 (s, *m*-Ph), 118.3 (d, $^1J_{C-P}$ = 15.1, *ipso*-Ph), 63.3 (s, $O\underline{C}H_2CH_3$), 24.5 (d, $^3J_{C-P}$ = 16.1, *o*-$\underline{C}H_3$Ph), 21.0 (s, *p*-CH_3Ph), 16.3 (d, $^3J_{C-P}$ = 5.0, $OCH_2\underline{C}H_3$). HRMS (methanol): found 447.12219, calcd 447.12312, $C_{17}H_{31}O_6P_3Na$, $[mol + Na]^+$.

Conversion of *P*,*P*-Dichlorophosphites into *P*,*P*-Dibromophosphites; General Procedure. To 1 equiv (0.79 g, 2.8 mmol of **2d** or 0.6 g, 4.6 mmol of **2e**) of *P*,*P*-dichlorophosphine was added dropwise 4 equiv (1.71 g, 11 mmol for **4d** or 2.81 g, 18.4 mmol for **4e**) of TMSBr at room temperature. The reaction mixture was stirred for 10 min before all volatilities were removed under vacuum (12 Torr) at room temperature, giving *P*,*P*-dibromophosphines **4d,e** as pale orange

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oils. Compounds **4** were pure by ^{1}H, ^{13}C, and ^{31}P NMR analysis and used in the next step without further purification.

***P,P*-Dibromo(TIPS-acetylene)phosphine (4d).** Yield: 0.93 g, 89%. ^{31}P ($CDCl_3$, {H}): 92.6. ^{1}H ($CDCl_3$): 1.11 (s, 21H, $Si(CH(CH_3)_2)_3$). ^{13}C ($CDCl_3$, {H}): 126.1 (d, $^{2}J_{C-P}$ = 3.01, −C≡C−P), 102.8 (d, $^{1}J_{C-P}$ = 91.5, −C≡C−P), 18.5 (s, $Si(CH(\underline{C}H_3)_2)_3$), 11.1 (d, $^{5}J_{C-P}$ = 2.0, $Si(\underline{C}H(CH_3)_2)_3$).

***P,P*-Dibromovinylphosphine (4e).** Yield: 0.92 g, 93%. ^{31}P ($CDCl_3$, {H}): 147.1. ^{1}H ($CDCl_3$): 7.17 (ddd, $^{3}J_{H-H}$ = 18.5, $^{2}J_{H-P}$ = 15.0, $^{3}J_{H-H}$ = 11.7, $PCHCH_2$), 6.02 (dd, $^{3}J_{H-H}$ = 18.5, $^{3}J_{H-P}$ = 18.5, $PCHC\underline{H}_2$), 5.89 (dd, $^{3}J_{H-P}$ = 43.2, $^{3}J_{H-H}$ = 11.7, $PCHC\underline{H}_2$). ^{13}C ($CDCl_3$, {H}): 139.8 (d, $^{1}J_{C-P}$ = 56.6, $P\underline{C}HCH_2$), 129.6 (d, $^{2}J_{C-P}$ = 44.0, $PCH\underline{C}H_2$).

Michaelis−Arbuzov Reaction of 4e,d with Triethylphosphite; General Procedure. One equivalent of *P,P*-dibromophosphine **4d,e** was dissolved in 5 mL of dry, oxygen-free toluene, and the resulting solution heated to 110 °C. Then 2 equiv of triethylphosphite was added in one portion to the refluxing solution of **4d,e**. Vigorous reaction with gas evolution started immediately. As soon as the color of the solution disappeared (ca. 5 min), heating was ceased. Removing of solvents under vacuum (1 Torr, heating bath from rt to 100 °C, 2 h) gave bis(*O,O*-diethyl)phosphonatophosphine as colorless oils. Compounds **3d,e** were pure by ^{1}H, ^{13}C, and ^{31}P NMR analysis and used in the next step without further purification.

Bis((*O,O*-diethyl)phosphonato)(TIPS-acetylene)phosphine (3d). **3d** was prepared according to the general procedure using 0.93 g (2.5 mmol) of **4e** and 0.83 g (5 mmol) of triethylphosphite. Yield: 1.09 g, 88%. ^{31}P ($CDCl_3$, {H}): 24.6 (d, $^{1}J_{P-P}$ = 155.4, P^{V}), −96.5 (t, P^{III}). ^{1}H ($CDCl_3$): 4.36−4.27 (m, 8H, $POC\underline{H}_2CH_3$), 1.38−1.34 (m, 12H, $POCH_2C\underline{H}_3$), 1.08 (bs, 21H, $Si(CH(CH_3)_2)_3$). ^{13}C ($CDCl_3$, {H}): 61.9 (d, $^{2}J_{C-P}$ = 6.0, $PO\underline{C}H_2CH_3$), 18.4 (d, $^{5}J_{C-P}$ = 2.0, $Si(CH(\underline{C}H_3)_2)_3$), 16.3 (d, $^{3}J_{C-P}$ = 7.0, $POCH_2\underline{C}H_3$), 10.9 (d, $^{4}J_{C-P}$ = 6.0, $Si(\underline{C}H(CH_3)_2)_3$). HRMS (methanol): found 509.1766, calcd 509.1783, $C_{19}H_{41}O_6P_3Si$ $[M + Na]^+$.

Bis((*O,O*-diethyl)phosphonato)vinylphosphine (3e). **3e** was prepared according to the general procedure using 0.92 g (4.3 mmol) of **4e** and 1.42 g (8.6 mmol) of triethylphosphite. Yield: 1.28 g, 95%. ^{31}P ($CDCl_3$, {H}): 29.0 (d, $^{1}J_{P-P}$ = 165.7, P^{V}), −68.7 (t, P^{III}). ^{1}H ($CDCl_3$): 6.60−6.64 (m, 1H, $PC\underline{H}CH_2$), 6.14−6.01 (m, 2H, $PCHC\underline{H}_2$), 4.25−4.16 (m, 8H, $OC\underline{H}_2CH_3$), 1.35−130 (m, 12H, $OCH_2C\underline{H}_3$). ^{13}C ($CDCl_3$, {H}): 136.4 (dt, $^{1}J_{C-P}$ = 32.2, $^{2}J_{C-P}$ = 15.1, $P\underline{C}HCH_2$), 123.2 (dt, $^{2}J_{C-P}$ = 16.1, $^{3}J_{C-P}$ = 5.0, $PCH\underline{C}H_2$), 63.5 (bs, $O\underline{C}H_2CH_3$), 16.4 (s, $OCH_2\underline{C}H_3$). HRMS (CH_3CN): found 333.07802, calcd 333.07857, $C_{10}H_{24}O_6P_3$ $[M + H]^+$.

Coordination to the Tungsten Core; General Procedure. $(CH_3CN)W(CO)_5$ was prepared in a modified literature procedure:[5,18] 1 equiv of $Me_3NO{\cdot}2H_2O$ was added in small portions over 20 min to a suspension of 1 equiv of tungstenhexacarbonyl in acetonitrile. During addition, the reaction temperature was kept below 10 °C. After gas evolution ceased and all precipitate was dissolved (ca. 30 min), the solvent was removed under vacuum, keeping the temperature of the bright yellow solution below 10 °C. The resulting solid $(CH_3CN)W(CO)_5$ was dried at high vacuum for 5 h. $(CH_3CN)W(CO)_5$ was then dissolved in THF and a solution of 1 equiv of diphosphonatophosphine **3a,b,d,e** in toluene was slowly added. The reaction mixture immediately turned dark green and was stirred at 40 °C for 10 h. Solvent was removed under vacuum, and the residue extracted with pentane (3 × 50 mL). The afforded bright yellow solution was concentrated under vacuum to give **5a,b,d,e** as yellow oils. The material was used for the next step without further purification.

Bis(*O,O*-diethyl)phosphonato)phenylphosphine Tungsten Pentacarbonyl (5a). Preparation according to the general procedure: 31.1 g (0.044 mol) of **3a**, 4.89 g (0.044 mol) of $Me_3NO{\cdot}2H_2O$, and 15.48 g (0.044 mol) of tungstenhexacarbonyl. The ^{31}P NMR of compound **5a** has been described in the literature[18] and is consistent with that found by us. Yield: 26.13 g, 84%. ^{31}P ($CDCl_3$, {H}): 20.0 (d, P^{V}), −19.5 (t, $^{1}J_{P-P}$= 65.9, $^{1}J_{P-W}$ = 225.4, P^{III}). ^{1}H ($CDCl_3$): 1.24 (m, 6H, CH_3), 1.34 (m, 6H, CH_3), 4.24 (m, 8H, CH_2), 7.17 (m, 1H, Ph), 7.24 ((m, 1H, Ph), 7.49 (m, 2H, Ph), 8.14 (m, 1H, Ph). ^{13}C ($CDCl_3$, {H}): 197.8 (d, $^{2}J_{C-P}$ = 26.1, CO), 195.7 (dt, $^{2}J_{C-P}$ = 6.0, $^{3}J_{C-P}$ = 2.0, $^{1}J_{C-W}$ = 125.3, CO), 134.8 (dt, $^{2}J_{C-P}$ = 12.1, $^{3}J_{C-P}$ = 5.0, *o*-Ph), 131.3 (dt, $^{4}J_{C-P}$ = 2.0, $^{5}J_{C-P}$ = 2.0, *p*-Ph), 128.8 (d, $^{3}J_{C-P}$ = 11.1, *m*-Ph), 124.7 (dt, $^{1}J_{C-P}$ = 39.2, $^{2}J_{C-P}$ = 2.0 *ipso*-Ph), 64.8 (d, $^{2}J_{C-P}$ = 3.0, CH_2), 64.7 (dd, $^{2}J_{C-P}$ = 4.0, $^{3}J_{C-P}$ = 1, CH_2), 64.5 (d, $^{2}J_{C-P}$ = 4.0, CH_2), 64.5 (d, $^{2}J_{C-P}$ = 4.0, CH_2), 16.3 (m, CH_3).

Bis(*O,O*-diethyl)phosphonato)tertbutylphosphine Tungsten Pentacarbonyl (5b). Preparation according to the general procedure: 4.51 g (12.5 mmol) of **3b**, 1.39 g (12.5 mmol) of $Me_3NO{\cdot}2H_2O$, and 4.40 g (12.5 mmol) of $W(CO)_6$. The ^{31}P NMR of compound **5a** has been described in the literature[18] and is consistent with that found by us. Yield: 5.93 g, 69%. ^{31}P ($CDCl_3$, {H}): 23.6 (d, P^{V}), 13.9 (t, $^{1}J_{P-P}$= 27.7, $^{1}J_{P-W}$= 213, P^{III}). ^{1}H ($CDCl_3$): 4.39−4.29 (m, 8H, $POC\underline{H}_2CH_3$), 1.50 (d, $^{2}J_{P-H}$ = 16.7, 9H, *t*-Bu), 1.38 (t, $^{3}J_{H-H}$ = 6.9, 6H, $POCH_2C\underline{H}_3$), 1.37 (t, $^{3}J_{H-H}$ = 6.9, 6H, $POCH_2C\underline{H}_3$). ^{13}C ($CDCl_3$, {H}): 197.5 (d, $^{2}J_{C-P}$ = 25.4, CO), 196.2 (dt, $^{2}J_{C-P}$ = 6.1, $^{3}J_{C-P}$ = 2.3, CO), 64.2 (dd, $^{2}J_{C-P}$ = $^{3}J_{C-P}$ = 3.9, $PO\underline{C}H_2CH_3$), 63.8 (dd, $^{2}J_{C-P}$ = $^{3}J_{C-P}$ = 3.9, $PO\underline{C}H_2CH_3$), 37.9 (dt, $^{1}J_{C-P}$ = 4.8, $^{2}J_{C-P}$ = 1.3, $\underline{C}(CH_3)_3$), 29.2 (dt, $^{2}J_{C-P}$ = 6.1, $^{3}J_{C-P}$ = 4.6, $C(\underline{C}H_3)_3$), 16.5−16.4 (m, $POCH_2\underline{C}H_3$).

Bis(*O,O*-diethyl)phosphonato)(TIPS-acetylene)phosphine Tungsten Pentacarbonyl (5d). Preparation according to the general procedure: 1.09 g (2.2 mmol) of **3d**, 0.28 (2.5 mmol) of $Me_3NO{\cdot}2H_2O$, and 0.88 g (2.5 mmol) of tungstenhexacarbonyl. Complex **5d** appears to be extremely moisture sensitive and could be isolated only in a mixture with 20% hydrolysis product, which we believe to be **9d** (^{31}P ($CDCl_3$, {H}): 16.3 (d, $^{1}J_{P-P}$ = 126.2, P^{V}), −103.0 (d, P^{III}). ^{31}P ($CDCl_3$): 16.3 (d, $^{1}J_{P-P}$ = 126.2, P^{V}), −103.0 (d, $^{1}J_{P-H}$ = 357.7 P^{III}).

5d. ^{31}P ($CDCl_3$, {H}): 15.3 (d, $^{1}J_{P-P}$ = 97.1, P^{V}), −61.7 (t, $^{1}J_{P-W}$ = 221.7, P^{III}). ^{1}H ($CDCl_3$): 4.46−4.25 (m, 8H, $POC\underline{H}_2CH_3$), 1.40−1.34 (m, 12H, $POCH_2C\underline{H}_3$), 1.10 (s, 21H, $Si(CH(CH_3)_2)_3$).

Bis((*O,O*-diethyl)phosphonato)vinylphosphine Tungsten Pentacarbonyl (5e). Preparation according to the general procedure: 1.28 g (4.1 mmol) of **3e**, 0.46 (4.1 mmol) of $Me_3NO{\cdot}2H_2O$, and 1.44 g (4.1 mmol) of tungstenhexacarbonyl. Yield: 1.6 g, 62%. ^{31}P (C_6D_6, {H}): 19.5 (d, $^{1}J_{P-P}$ = 79.3, P^{V}), −28.3 (t, $^{1}J_{P-W}$ = 223.3, P^{III}). ^{1}H (C_6D_6): 6.58 (dddt, $^{3}J_{H-H}$ = 18.1, $^{2}J_{H-P}$ = 13.9, $^{3}J_{H-H}$ = 11.6, $^{3}J_{H-P}$ = 6.0, 1H, $PC\underline{H}CH_2$), 6.17 (ddt, $^{3}J_{H-P}$ = 21.1, $^{3}J_{H-H}$ = 18.1, $^{4}J_{P-H}$ = 2.8, 1H, $PCHC\underline{H}_2$), 5.71 (dd, $^{3}J_{H-P}$ = 44.9, $^{3}J_{H-H}$ = 11.6, 1H, $PCHC\underline{H}_2$), 4.28−4.07 (m, 8H, $OC\underline{H}_2CH_3$), 1.08 (t, $^{3}J_{H-H}$ = 7.1, $OCH_2C\underline{H}_3$), 1.04 (t, $^{3}J_{H-H}$ = 7.1, $OCH_2C\underline{H}_3$). ^{13}C (C_6D_6, {H}): 198.0 (d, $^{2}J_{C-P}$ = 25.8, CO), 195.8 (dt, $^{2}J_{C-P}$ = 6.0, $^{3}J_{C-P}$ = 2.0, CO), 137.3 (dt, $^{2}J_{C-P}$ = 9.0, $^{3}J_{C-P}$ = 9.0, $PCH\underline{C}H_2$), 125.3 (d, $^{1}J_{C-P}$ = 25.2, $P\underline{C}HCH_2$), 64.6 (d, $^{2}J_{C-P}$ = 7.3, $O\underline{C}H_2CH_3$), 64.6 (d, $^{2}J_{C-P}$ = 6.9, $O\underline{C}H_2CH_3$), 16.3 (dd, $^{3}J_{C-P}$ = 3.0, $^{4}J_{C-P}$ = 3.0, $OCH_2\underline{C}H_3$), 16.2 (dd, $^{3}J_{C-P}$ = 3.2, $^{4}J_{C-P}$ = 3.2, $OCH_2\underline{C}H_3$). HRMS (methanol): found 678.9847, calcd 678.9860, $C_{15}H_{23}O_{11}P_3WNa$ $[M + Na]^+$. IR (solution in pentane, cm^{-1}): 2078, 1983, 1960, 1379, 1267, 1251, 1163, 1032, 1018.

Synthesis of 9a,b; General Procedure. A solution of compound **5a,b** (26.13 g, 0.037 mol of **5a** and 5.93 g, 8.6 mmol of **5b**) in THF (250 mL) was cooled to −30 °C, and 1 equiv (74 mL for **5a** and 17.3 mL for **5b**) of a 0.5 M solution of sodium methanolate in methanol was added dropwise over 20 min. The reaction mixture was stirred at −30 °C for 30 min and quenched by the addition of a 10% solution of ammonium chloride (100 mL). Once the mixture reached room temperature, the phases were separated and the water phase extracted three times with 100 mL of diethyl ether. Combined organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed under vacuum, and the residue chromatographed on silica gel (Merck, grade 7734, mesh 70−230) using a diethyl ether/pentane, 1:1, mixture as eluent to give phosphinophosphonates **9a,b** as a white solid.

Alternatively, **5a** can be dissolved in pentane and chromatographed on Al_2O_3 using diethyl ether/pentane, 1:1, as eluent, affording **9a**, however in lower overall yield of 40% over three steps. Analytical data are consistent with those described in the literature.[5]

(*O,O*-Diethyl)phosphonato)phenylphosphine Tungsten Pentacarbonyl (9a). Yield: 15.6 g, 75%. ^{31}P ($CDCl_3$, {H}): 21.9 (d, P^{V}), −49.0 (d, $^{1}J_{P-P}$ = 79.8, $^{1}J_{P-W}$ = 225.4, P^{III}). ^{1}H ($CDCl_3$): 1.24 (t, $^{3}J_{H-H}$ = 7.3, 3H, CH_3), 1.25 (t, $^{3}J_{H-H}$ = 7.0, 3H, CH_3), 4.05 (m, 4H,

CH_2), 5.99 (d, $^1J_{H-P}$= 338.0, 1H, H−P), 7.47 (m, 3H, Ph), 7.68 (m, 2H, Ph). ^{13}C ($CDCl_3$, {H}): 197.7 (d, $^2J_{C-P}$ = 23.1, CO), 195.0 (dd, $^2J_{C-P}$ = 7.0, $^3J_{C-P}$ = 3.0, $^1J_{C-W}$ = 126.7, CO), 133.7 (dd, $^2J_{C-P}$ = 11.1, $^3J_{C-P}$ = 4.0, *o*-Ph), 131.3 (dd, $^4J_{C-P}$ = 2.0, $^5J_{C-P}$ = 2.0, *p*-Ph), 129.2 (dd, $^3J_{C-P}$ = 10.1, $^4J_{C-P}$ = 2.0, *m*-Ph), 125.3 (d, $^1J_{C-P}$ = 39.2, *ipso*-Ph), 64.1 (d, $^2J_{C-P}$ = 8.0, CH_2), 63.8 (d, $^2J_{C-P}$ = 8.0, CH_2), 16.3 (d, $^3J_{C-P}$ = 2.0, CH_3), 16.2 (d, $^3J_{C-P}$ = 2.0, CH_3). IR (solution in pentane, cm^{-1}): 2078, 1990, 1952, 1921, 1257(P═O), 1041, 1017, 967(P−H).

(*O,O*-Diethyl)phosphonato)tertbutylphosphine Tungsten Pentacarbonyl (9b). Yield: 2.58 g, 57%. ^{31}P ($CDCl_3$, {H}): 24.0 (d, $^1J_{P-P}$ = 43.7, P^V), −18.2 (d, $^1J_{P-W}$ = 216.9, P^{III}). ^1H ($CDCl_3$): 4.92 (d, $^1J_{H-P}$ = 315.8, 1H, HP), 4.29−4.17 (m, 4H, OCH_2CH_3), 1.43 (dd, $^3J_{H-P}$ = 16.79, $^4J_{H-P}$ = 0.8, 9H, *t*-Bu), 1.38 (t, $^3J_{H-H}$ = 6.79, 3H, OCH_2CH_3), 1.37 (t, $^3J_{H-H}$ = 6.79, 3H, OCH_2CH_3). ^{13}C ($CDCl_3$, {H}): 197.7 (d, $^2J_{C-P}$ = 24.1, CO), 195.9 (dd, $^2J_{C-P}$ = 7.0, $^3J_{C-P}$ = 3.0, CO), 63.4 (d, $^3J_{C-P}$ = 7.0, OCH_2CH_3), 62.8 (dd, $^3J_{C-H}$ = 8.0, $^4J_{C-P}$ = 1, OCH_2CH_3), 33.5 (dd, $^1J_{C-P}$ = 18.1, $^2J_{C-P}$ = 2.0, $PC(CH_3)_3$), 29.7 (dd, $^2J_{C-P}$= $^3J_{C-P}$ = 5.0, $PC(CH_3)_3$), 16.4 (d, $^3J_{C-P}$ = 1.3, OCH_2CH_3), 16.3 (d, $^3J_{C-P}$ = 1.6, OCH_2CH_3). IR (solution in pentane, cm^{-1}): 2076, 1984, 1950, 1930, 1910, 1379, 1251, 1043, 1018.

Hydrolysis of 5d. A 2.1 g (2.2 mmol) portion of the reaction mixture from the previous step was dissolved in 25 mL of THF and stirred open to air for 30 min. Solvents were removed under vacuum, and the resulting oily residue was dissolved in diethyl ether, which was directly transferred to a silica gel column. Side products were washed with diethyl ether. Target complex **10d** was recovered with 10% methanol in diethyl ether and obtained as a pale yellow solid.

10d. Yield: 0.3 g, 20%. ^{31}P (CD_3OD, {H}): 37.2 (d, $^1J_{P-P}$ = 89, P^V), −138.7 (d, $^1J_{P-W}$ = 195.8, P^{III}). ^1H (CD_3OD): 4.23 (dq, $^2J_{P-H}$ = 8.0, $^3J_{H-H}$ = 8.0, 4H, OCH_2CH_3), 1.31 (t, $^3J_{H-H}$ = 8.0, 6H, OCH_2CH_3), 1.10 (s, 21H, TIPS). ^{13}C (CD_3OD, {H}): 203.4 (d, $^2J_{C-P}$ = 15.1, CO), 200.7 (dd, $^2J_{C-P}$ = 4.0, $^3J_{C-P}$ = 4.0, $^1J_{C-W}$ = 127.7, CO), 109.2 (d, $^1J_{C-P}$ = 11.1, −C≡C-P), 106.6 (dd, $^2J_{C-P}$ = 10.1, $^3J_{C-P}$ = 8.0, −C≡C−P), 63.6 (d, $^2J_{C-P}$ = 8.0, OCH_2CH_3), 19.2 (s, $Si(CH(CH_3)_2)_3$), 16.8 (d, $^3J_{C-P}$ = 6.0, OCH_2CH_3), 12.8 (s, $Si(CH(CH_3)_2)_3$). HRMS (ACN solution): found 713.07005, calcd 713.06978, $C_{20}H_{32}O_9P_2SiWNa$, [M − H + NaOH]$^+$. IR (solution in methanol, cm^{-1}): 2068, 2057, 1944, 1917, 1891.

Hydrolysis of 5e. A 1.6 g (2.5 mmol) amount of **5e** was dissolved in 25 mL of THF and cooled to −25 °C. After this, 6.3 mL (3.1 mmol, 0.5 M solution in methanol) of a sodium methoxide solution was added dropwise. The reaction mixture was stirred for 30 min and quenched with water. The resulting solution was allowed to warm to rt, and organic solvents were removed under vacuum. The residue was extracted with diethyl ether (3 × 25 mL). The organic washings were combined, washed with brine, and dried over magnesium sulfate. Solvent was removed to leave 5 mL of solution, which was directly applied to a silica gel column. Small amounts of byproducts were washed with diethyl ether. **10e** was washed with a solution of 20% methanol in diethyl ether. **11e** was washed from the column with pure methanol. Removal of the solvent resulted in a yellow oil, which upon treatment with pentane afforded a pale yellow precipitate of **11e**.

When the reaction mixture after sodium methoxide treatment was quenched with an aqueous solution of *p*-toluenesulfonic acid (2 equiv), **9e** was the only product formed (as detected by NMR). The separated organic layer was dried over magnesium sulfate, and the solvent removed under vacuum to afford crude **9e**. **9e** is unstable under chromatography conditions and slowly polymerizes.

(*O,O*-Diethyl)phosphonatovinylphosphine Tungsten Pentacarbonyl (9e). ^{31}P ($CDCl_3$, {H}): 21.7 (d, $^1J_{P-P}$ = 95.5, P^V), −60.8 (d, $^1J_{P-W}$ = 225, P^{III}). ^{31}P ($CDCl_3$): 21.7 (d, $^1J_{P-P}$ = 95.5, P^V), −60.8 (dm, $^1J_{H-P}$ = 336, P^{III}). ^1H ($CDCl_3$): 6.50−6.33 (m, 1H, $PCHCH_2$), 6.25−6.06 (m, 2H, $PCHCH_2$), 5.59 (dd, $^1J_{H-P}$ = 336.2, $^3J_{H-H}$ = 5.9, PH), 4.31−4.18 (m, 4H, OCH_2CH_3), 1.38 (t, $^3J_{H-H}$ = 6.8, 3H, OCH_2CH_3), 1.36 (t, $^3J_{H-H}$ = 6.8, 3H, OCH_2CH_3).

10e. Yellow solid. Yield: 0.14 g, 10%. ^{31}P (CD_3OD, {H}): 43.9 (d, $^1J_{P-P}$ = 111.7, P^V), −96.6 (d, $^1J_{P-W}$ = 161.8, P^{III}). ^1H (CD_3OD): 6.68 (dddd, $^3J_{H-H}$ = 18.0, $^2J_{H-P}$ = 14.4, $^3J_{H-H}$ = 11.4, $^3J_{H-P}$ = 10.5, 1H, $PCHCH_2$), 5.62 (dddd, $^3J_{H-H}$ = 18.0, $^3J_{H-P}$ = 17.9, $^4J_{H-P}$ = 3.1, $^2J_{H-H}$ = 1.5, 1H, $PCHCH_2$), 5.50 (ddd, $^3J_{H-P}$ = 36.2, $^3J_{H-H}$ = 11.4, $^2J_{H-H}$ = 1.5, 1H, $PCHCH_2$), 4.13 (pentet, $^3J_{H-H}$ = $^3J_{H-P}$ = 7.1, 4H, OCH_2CH_3), 1.30 (t, $^3J_{H-H}$ = 7.1, 6H, OCH_2CH_3). HRMS (CH_3CN): found 558.9519, calcd 558.9520, $C_{11}H_{14}O_9P_2WNa$, [M − H + NaOH]$^+$. IR (solution in methanol, cm^{-1}): 2069, 2054, 1940, 1916, 1892.

1,4-(*O,O*-Diethyl)diphosphonate-1,4-diphosphinane Tungsten Pentacarbonyl (11e). Yellow solid. Yield: 0.33 g, 25%. ^{31}P ($CDCl_3$), {H}): 24.4 (d, $^1J_{P-P}$ = 76.1, P^V), −27.5 (dd, $^1J_{P-P}$ = 76.1, $^3J_{P-P}$ = 6.5, ^{III}P), −27.4 (dd, $^1J_{P-P}$ = 76.1, $^3J_{P-P}$ = 6.5, ^{III}P). ^1H ($CDCl_3$): 4.31 (dq, $^2J_{H-P}$ = 8.7, $^3J_{H-H}$ = 7.1, 8H, OCH_2CH_3), 3.17−2.94 (m, 4H, PCH_2), 2.41−2.20 (m, 4H, PCH_2), 1.40 (t, $^3J_{H-H}$ = 7.1, OCH_2CH_3). ^{13}C ($CDCl_3$, {H}): 197.2 (d, $^2J_{C-P}$ = 23.1, CO), 195.5 (d, $^2J_{C-P}$ = 2, $^1J_{C-W}$ = 125.7, CO), 195.4 (d, $^2J_{C-P}$ = 2, $^1J_{C-W}$ = 124.7, CO), 63.8 (d, $^2J_{C-P}$ = 8.0, OCH_2CH_3), 22.0 (dd, $^1J_{C-P}$ = 15.9, $^2J_{C-P}$ = 3.8, PCH_2), 21.9 (dd, $^1J_{C-P}$ = 16.3, $^2J_{C-P}$ = 3.4, PCH_2), 16.6 (d, $^3J_{C-P}$ = 5.0, OCH_2CH_3). HRMS (CH_3OH): found 1062.9248, calcd 1062.9244, $C_{22}H_{28}O_{16}P_4W_2Na$, [M + Na]$^+$.

Reaction of 9a with Acetone. A 0.84 g (1.5 mmol) sample of **9a** was dissolved in 15 mL of THF and cooled to −10 °C. Then 0.75 mL of a 2 M solution of LDA was added dropwise. The reaction mixture changed color to bright yellow. Formation of the lithium salt **8a-Li** was confirmed by ^{31}P NMR (63.8 (d, J^1_{P-P} = 381 Hz), −106.4 (d, J^1_{P-W} = 98 Hz)).[5] The reaction mixture was then cooled to −78 °C, and 5 equiv of dry acetone was added. The reaction mixture was warmed to room temperature and stirred for 6 h. Solvent removal under vacuum resulted in a yellow residue, which was purified by column chromatography on silica gel using diethyl ether/pentane, 1:9, as eluent. The simultaneous formation of **12** and **13** was observed. If the reaction mixture was stirred for longer times (15−24 h), only **13** was obtained. The analytical data for **12** are in accordance with the literature data.[4]

Diphosphitane 13. Colorless oil that solidifies in the freezer. Yield: 0.38 g, 53%. ^{31}P ($CDCl_3$, {H}): 121.4 ($^1J_{P-W}$ = 267.0). ^1H ($CDCl_3$): 7.57−7.40 (m, 5H, Ph), 1.20 (dd, $^3J_{P-H}$ = 16.0, $^4J_{P-H}$ = 8.0, 6H, CH_3), 1.03 (dd, $^3J_{P-H}$ = 16.0, $^4J_{P-H}$ = 4.0, 6H, CH_3). ^{13}C ($CDCl_3$, {H}): 198.8 (d, $^2J_{C-P}$ = 22.1, CO), 196.6 (d, $^2J_{C-P}$ = 7.0, $^1J_{C-W}$ = 125.3), 139.6 (d, $^1J_{C-P}$ = 39.2, *ipso*-Ph), 130.3 (d, $^4J_{C-P}$ = 3.0, *p*-Ph), 128.6 (d, $^2J_{C-P}$ = 13.1, *o*-Ph), 128.4 (d, $^3J_{C-P}$ = 10.1, *m*-Ph), 36.9 (d, $^1J_{C-P}$ = 28.2), 16.7 (d, $^3J_{C-P}$ = 4.0, CH_3), 16.2 (s, CH_3). HRMS (solution in methanol with addition of $AgOOCF_3$): 1092.89844, calcd 1092.90034, $C_{28}H_{22}O_{10}P_2W_2(H_2O)_2Ag$. IR (solution in pentane, cm^{-1}): 2073, 1981, 1957, 1946, 1930, 1108, 1034, 1010.

***In Situ* Generation of 8e-Li and Its Reaction with Acetone.** A 0.203 g (0.3 mmol) amount of **5e** was dissolved in 5 mL of THF, and 0.16 mL (0.3 mmol, 2 M solution in methanol) of lithium methoxide solution was added at rt. The reaction mixture was stirred for 10 min, and an aliquot taken for NMR showed complete formation of **8e-Li**. **8e-Li**: ^{31}P (THF/methanol, C_6D_6 as internal locking standard, {H}): 63.44 (d, $^1J_{P-P}$ = 350.3, P^V), −113.1 (d, $^1J_{P-W}$ = 97.1, P^{III}). After this 0.1 mL of dry acetone was added to the reaction mixture, and the resulting solution stirred for 8 h at room temperature. Solvents were removed under vacuum, and the yellow, oily residue was chromatographed on silica gel using pentane as eluent (R_f = 0.4). **16** was obtained as a colorless oil.

16. Yield: 0.041 g, 28%. ^{31}P ($CDCl_3$, {H}): 137.8 ($^1J_{P-W}$ = 270.3). ^1H ($CDCl_3$): 6.24 (ddd, $^2J_{H-P}$ = 23.2, $^3J_{H-H}$ = 18.0, $^3J_{H-H}$ = 12.2, 1H, $PCHCH_2$), 6.04 (dd, $^3J_{H-P}$ = 34.9, $^3J_{H-H}$ = 12.2, 1H, $PCHCH_2$), 5.87 (dd, $^3J_{H-H}$ = 18.0, $^3J_{H-P}$ = 18.0, 1H, $PCHCH_2$), 3.51 (d, $^2J_{H-P}$ = 12.5, 3H, OCH_3), 2.29−2.17 (m, 1H, $PCH(CH_3)_2$), 1.17 (dd, $^3J_{H-P}$ = 17.6, $^3J_{H-H}$ = 7.3, 3H, $PCH(CH_3)_2$), 1.10 (dd, $^3J_{H-P}$ = 17.8, $^3J_{H-H}$ = 7.3, 3H, $PCH(CH_3)_2$). ^{13}C ($CDCl_3$, {H}): 198.6 (d, $^2J_{C-P}$ = 24.2, CO), 196.5 (d, $^2J_{C-P}$ = 7.7, $^1J_{C-W}$ = 125.7, CO), 135.9 (d, $^1J_{C-P}$ = 29.2, $PCHCH_2$), 131.6 (d, $^2J_{C-P}$ = 4.7, $PCHCH_2$), 54.5 (d, $^2J_{C-P}$ = 4.3, OCH_3), 34.2 (d, $^1J_{C-P}$ = 32.4, $PCH(CH_3)_2$), 16.5 (d, $^2J_{C-P}$ = 3.8, $PCH(CH_3)_2$), 15.9 (d, $^2J_{C-P}$ = 4.7, $PCH(CH_3)_2$). HRMS (solution in mixture of methanol and chloroform): found 918.00045, calcd 917.99999, $C_{22}H_{25}O_{12}P_2W_2Li$, Coulomb dimer [$M_2$ − H + Li]$^+$. IR (solution in pentane, cm^{-1}): 2073, 1979, 1955, 1944, 1914, 1379, 1033.

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■ ASSOCIATED CONTENT

Supporting Information

Summary of the X-ray data of **9a** and copies of the NMR spectra.This material is available free of charge via the Internet at http://pubs.acs.org.

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