Reactivity of (Phosphaalkenyl)metal Species: Transmetalations and Reactions with Carbonyl Compounds†

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The (phosphaalkenyl)lithium carbenoid (*Z*)-Mes*P═CClLi (**2**; Mes* = supermesityl = 2,4,6-tri-*tert*-butylphenyl) was transmetalated with $MgBr_2$, $ZnCl_2$, and $HgCl_2$ to furnish the new (phosphavinylidene)metal carbenoids Mes*P═CClMX ((*Z*)-**5a**, MX = MgBr; (*E*)-**5b**, MX = ZnCl; (*E*)-**5c**, MX = HgCl), while with 0.5 equiv of the metal halide, the bis(phosphaalkenyl)-metal carbenoids $(Mes*P═CCl)_2M$ ((*Z*,*Z*)-**6a**, M = Mg; (*E*,*E*)-**6b**, M = Zn; (*E*,*E*)-**6c**, M = Hg) were formed. Compounds **2** and **5a** were reacted with carbonyl compounds under 1,2-addition, leading to the β-phosphaallyl alcohols **7**−**10**. Bromine−lithium exchange at −90 °C between (*Z*)-Mes*P═CBrSiMe$_3$ ((*Z*)-**14**) and *n*-butyllithium furnished (*E*)-/(*Z*)-Mes*P═CLiSiMe$_3$ ((*E*)-/(*Z*)-**16**; *E*:*Z* = 1:1. Transmetalation of (*E*)-/(*Z*)-**16** with $MgBr_2$ or $ZnCl_2$ furnished only the *trans*-metal isomer of Mes*P═CMXSiMe$_3$ ((*Z*)-**18a**, MX = MgBr; (*E*)-**18b**, MX = ZnCl). From (*E*)-/(*Z*)-**16**, a new access to the phosphaallene Mes*P═C═CPh$_2$ (**20**) was obtained by reaction with benzophenone.

Introduction

During the last three decades, considerable progress has been made in the synthesis of various phosphaalkenes.[1] In the vast majority of approaches, the phosphaalkene was obtained by introduction of the P═C moiety in the final step through an elimination reaction of an appropriate precursor. This method usually gives mixtures of the two isomers of the phosphaalkene, which limits this synthetic application. Since 1981, methods have been developed for the synthesis of halogen-substituted phosphaalkenes;[2−6] these permit a different approach by chemical variation of the substitution pattern with retention of the P═C unit. Thus, *C*-halogen-substituted phosphaalkenes (Mes*P═CX$_2$; Mes* = 2,4,6-tri-*tert*-butylphenyl, X = Cl, Br, I) have been investigated with the aim of using their potential as key synthons for the preparation of functionalized phosphaalkenes via halogen−metal exchange with *n*-butyllithium under formation of the versatile organolithium reagents. Several examples of the use of these organolithium reagents have been reported.[2a,2c,5−8]

Usually these phosphaalkenes bear the supermesitylene (Mes*) group at phosphorus for two reasons. First, the lithiation of the halogen-substituted phosphaalkenes selectively takes place at the position *trans* to the Mes* group;[2a,c,5−8] this is probably due to steric hindrance. Derivatization of the lithium carbenoid normally occurs stereospecifically to furnish the *trans* products. This selective *trans* functionalization attracted our attention because of the possible utilization for the the synthesis of phosphaalkene-based ligand systems, wherein the phosphorus center is one of the coordinating sites; recently new developments in this area have been reported.[9] Second, the P═C unit in the resulting phosphaalkenes is very stable toward heat, moisture, and oxygen. The selective formation of isomerically pure and stable phosphaalkenes makes the spectroscopic study of these species possible, which will lead to a better understanding of the characteristics of phosphaalkenes.[8]

A practical difficulty with lithium carbenoids is their low thermal stability.[10] The stability of carbenoids depends on the halogen and the metal, and it increases in the order I < Br < Cl[11] and Li < Mg < Zn < Hg.[10] Organolithium compounds including lithium carbenoids are known to be easily transmetalated by more elec-

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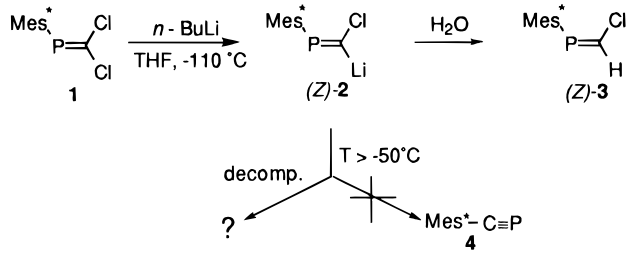
Scheme 1



tronegative metals such as magnesium, zinc, mercury, and silicon.[10] Transmetalation is expected to lead to more stable organometallic species which should be more convenient to handle.

In this article, we present the synthesis and stability of new (phosphavinylidene)magnesium, -zinc, and -mercury carbenoids. The difference in reactivity between the lithium and magnesium carbenoids has been investigated by reaction with carbonyl compounds such as benzaldehyde, benzophenone, acetophenone, and crotonaldehyde leading to 3-phosphaallylic alcohols, and with acetyl chloride leading to a β-phosphaenone.[8] Simultaneously and independently Yoshifuji *et al.* have investigated this synthetic approach to functionalized phosphaalkenes.[6c]

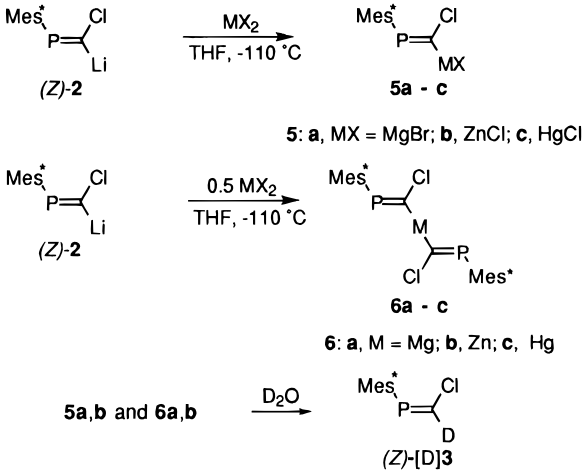
Furthermore, we attempted to convert the [(*Z*)-bromophosphaalkenyl]lithium carbenoid into a *trans*-(trimethylsilyl)phosphaalkene, a phosphaalkene with an expected high potential for further functionalization. However, during this research we discovered a very rapid isomerization in the intermediate α-lithio(trimethylsilyl)phosphaalkene. We will discuss the synthesis and thermal and configurational stability of α-metallo(trimethylsilyl)phosphaalkenes of lithium, magnesium, and zinc. The α-lithio(trimethylsilyl)phosphaalkene was applied in a novel and rapid synthetic route to a phosphaallene.

Synthesis and Transmetalation Reactions of the (Phosphaalkenyl)lithium Carbenoid 2

Halogen−metal exchange of dichlorophosphaalkene **1** with *n*-butyllithium at −110 °C selectively lithiates **1** at the position *trans* to the Mes* group to give (*Z*)-**2**. The selectivity of this reaction was proven by hydrolysis; it furnishes (*Z*)-**3**[6b] with the hydrogen *trans* to the Mes* group only (Scheme 1). The quantitative formation of only one isomer of **3** proves the configurational stability of the lithium carbenoid **2**; it is stable at temperatures below −50 °C. At higher temperatures **2** decomposes with formation of as yet unknown products. The phosphaacetylene decomposition product **4** was not formed, as has already been noted by Yoshifuji *et al.*[6b]

In order to study the dependence of the stability and the reactivity of α-chlorophosphavinylidene carbenoids on the metal, we prepared the magnesium, zinc, and mercury carbenoids **5a**−**c** by transmetalation reactions of **2** with 1 equiv of magnesium bromide, zinc chloride, or mercury(II) chloride, respectively (Scheme 2). The addition of a solution of 1 equiv of the metal halide to **2** at −110 °C in THF solution quantitatively furnished the

Scheme 2



metal carbenoids **5a**−**c** after warming the reaction mixtures to 15 °C (**5a**) or room temperature (**5b**,**c**). The successful transformation of **2** to **5a**,**b** followed from the high thermal stability of the products; the quantitative formation and configurational stability of the magnesium and zinc carbenoids **5a**,**b** was proven by deuterolysis followed by isolation of the deuterated monochlorophosphaalkene (*Z*)-[D]**3**. After workup, (*Z*)-[D]**3** was almost quantitatively isolated in >95% yield. (*Z*)-[D]**3** was characterized by ^{1}H and ^{31}P NMR spectroscopy. The spectroscopic data for (*Z*)-[D]**3** were identical with those for (*Z*)-**3**[2b,c] with the exception of the characteristic vinylic proton signal (δ(^{1}H) 6.9; ^2J(HP) = 47 Hz). In both cases no (*E*)-[D]**3** was formed; this proves the configurational stability of **5a**,**b**. In case of the mercury carbenoid **5c** (δ(^{31}P) 281; 86%), air-stable crystals were obtained which could be characterized without deuterolysis (Scheme 2).

Analogously, the addition of 0.5 equiv of the metal halide furnished a solution of the bis(phosphavinylidene)metal carbenoid species **6a**−**c**. Deuterolysis of **6a**,**b** proved their formation and configurational stability. The mercurio analogue **6c** (δ(^{31}P) 277; 90% yield) was isolated as air-stable crystals.

As phosphaalkenes **5c** and **6c** could not be hydrolyzed to furnish **3**, no direct evidence was obtained for the assignment of their configuration. However, making use of the empirical "*cis* rule", the product configuration can be determined as being that of (*E*)-mercurio phosphaalkenes. Goede *et al.* found a large difference in the ^2J(PHg) coupling constants for *E* and *Z* isomers of analogous mercuriophosphaalkenes: (*E*)- and (*Z*)-(chloromercuriomethylene)(2,4,6-tri-*tert*-butylphenyl)phosphane (^2J(PHg) = 1365 and 368 Hz, respectively) and (*E*,*E*)- and (*Z*,*Z*)-mercuriobis[methylene(2,4,6-tri-*tert*-butylphenyl)phosphane] (^2J(PHg) = 805 and 182 Hz, respectively].[12] Both **5c** (^2J(PHg) = 1439 Hz) and **6c** (J(PHg) = 993 Hz) show a large coupling and are therefore assigned the *E* configuration. In contrast to (*E*,*E*)-mercuriobis[methylene(2,4,6-tri-*tert*-butylphenyl)-phosphane], which shows isomerization to the *Z*,*Z* isomer (by an unknown mechanism),[12] (*E*,*E*)-**6c** appears to be configurationally stable.

The stability order of the newly formed phosphavinylidene carbenoids corresponds to the expected se-

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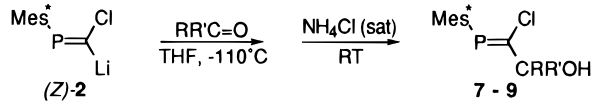
Scheme 3



7: R = H, R' = Ph; **8**: R = R' = Ph; **9**: R = H, R' = *(E)* - CH=CHMe

quence Li < Mg < Zn < Hg. Whereas **2** decomposes at temperatures above −50 °C, the magnesium carbenoids **5a** and **6a** slowly decompose at 15 °C. As in the case of **2**, the formation of **4** was not observed. Neither **4** nor any other phosphorus-containing product could be detected in the ^{31}P NMR spectrum, so that at present, the mode of decomposition of **5a** and **6a** is unclear. The zinc carbenoids **5b** and **6b** are stable at room temperature for at least a few days; as in the case of **5a** and **6a**, the decomposition products are unknown. The mercury carbenoids **5c** and **6c** are the most stable ones; the white, air-stable crystals can be stored at room temperature in the air.

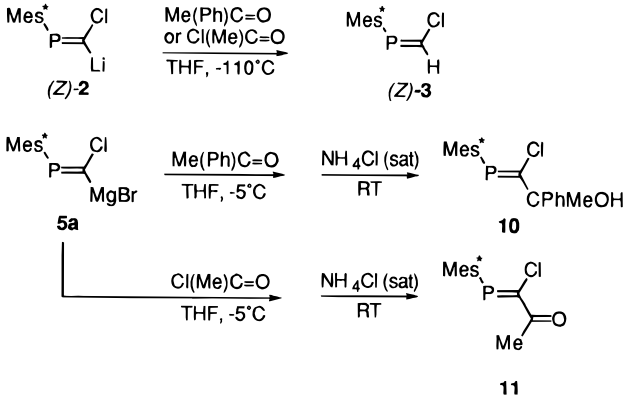
Reactivity of α-Chlorophosphavinylidene Carbenoids with Carbonyl Compounds

In view of the wide use of organolithium compounds in reactions with carbonyl groups,[13] we scanned the analogous applicability of **2**. The transmetalation product **5a** was included in order to study possible differences in reactivity between **2** and **5a**. Because of the relative inertness of organozinc and organomercury species toward carbonyl compounds (no reaction was observed between **5b**,**c** and benzaldehyde), the reactivity of **5b**,**c** was not further investigated.

Carbenoid **2** was reacted with various carbonyl compounds such as ketones, aldehydes, and α,*β*-unsaturated aldehydes (Scheme 3). The only ester included in this investigation was methyl benzoate; according to the ^{31}P NMR spectra, it gave rise to a great number of phosphorus signals in the region from +331 to −17 ppm; for that reason the reactivity with esters was not further explored. Secondary and tertiary *β*-phosphaallylic alcohols **7** and **8** were synthesized by the reaction of **2** with benzaldehyde and benzophenone, respectively; hydrolytic workup at room temperature furnished the alcohols in high yield (94−95%). The reaction with crotonaldehyde selectively proceeded by 1,2-addition, leading to the secondary alcohol **9** after hydrolytic workup (yield: 77%).

Carbenoids **2** and **5a** were both reacted with acetophenone (Scheme 4). Addition of acetophenone to **2** did not furnish the corresponding tertiary alcohol **10**. Only (*Z*)-**3** was isolated, which indicates that **2** is too strongly basic to undergo nucleophilic attack on the carbonyl group of an enolizable carbonyl compound such as acetophenone. This limitation narrows the scope of the utility of **2** considerably. Fortunately, the use of magnesium carbenoid **5a** allows us to circumvent this problem. Addition of 1 equiv of acetophenone to a solution of **5a** furnished 75% of the desired tertiary alcohol **10** and 25% of the deprotonation product (*Z*)-**3**. Compound **10** was isolated as a yellow oil after column chromatography. A second example of the lower basicity of **5a** compared to that of **2** is the difference in

Scheme 4



reactivity with acetyl chloride: with **2**, (*Z*)-**3** was the only product, but the addition of acetyl chloride to **5a** at −5 °C furnished phosphaenone **11** in 60% yield. The infrared spectrum of **11** showed a characteristic C=O stretching frequency at 1667 cm^{-1}, which is in the expected range for a (*β*-phospha) α,*β*-unsaturated ketone.[8]

An interesting aspect of the introduction of a chiral center at the phosphaallylic position is the appearance of two ^{1}H NMR signals of the *o*-*tert*-butyl substituents of the Mes* group in **7**, **9**, and **10**, whereas normally, only one signal is observed. To our knowledge, this is the first time this has been observed in phosphaalkene chemistry. The appearance of two diastereotopic *tert*-butyl groups implies a slow rotation around the C(Mes*)−P bond on the NMR time scale. The ^{1}H NMR spectra were unchanged when **7** was heated to 70 °C.

Synthesis and Configurational Stability of α-Metallo(trimethylsilyl)phosphaalkenes

Although the relatively stable phosphavinylidene carbenoids **5a** and **6a** are easily accessible, their stability is limited at elevated temperatures (T > 15 °C). This is detrimental to their application in C−C coupling reactions such as palladium(0)-catalyzed Stille type coupling reactions, because these require higher temperatures and do not tolerate α-halogens because of carbenoid type palladium halide elimination.[14] Therefore, the synthesis of a both stable and sufficiently reactive *trans* metal or metalloid phosphaalkene species with a non-halogen group at the *cis* position relative to the Mes* group is of interest. Although such species have been synthesized before,[12] the pure (*trans*) species were not available. A possible access was envisaged by starting from the bromo trimethylsilyl substituted phosphaalkene (*Z*)-**14**, earlier described by Appel *et al.*[2c] (Scheme 5). Bromine−lithium exchange and subsequent protonation would lead to the *trans*-trimethylsilyl-substituted phosphaalkene (*E*)-**17**, which should be a convenient starting point for further functionalization.

Dibromophosphaalkene **12**[2c,4b,5] was synthesized on a large scale by a new convenient route. It consists of addition of 2 equiv of *n*-butyllithium to a mixture of Mes*PCl_2 and tetrabromomethane at low temperature

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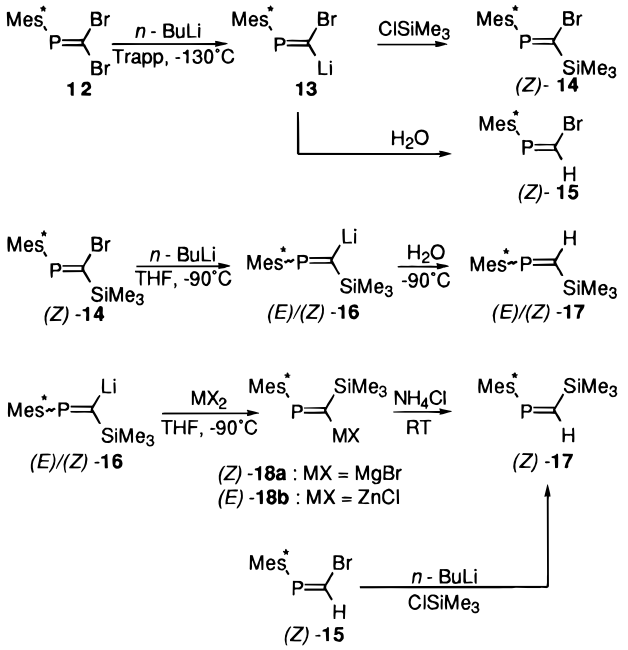
Scheme 5



in THF solution; this method was inspired by the synthesis of the diiodophosphaalkene from Mes*PCl_2 and tetraiodomethane developed by Goede *et al.*[5] Compound **12** was lithiated by *n*-butyllithium at −130 °C using the Trapp mixture[15] in order to achieve the highest possible selectivity in *trans* lithiation. The intermediate carbenoid **13** was reacted with trimethylsilyl chloride, furnishing (*Z*)-**14** in 98% isomeric purity, contaminated with 2% of the *E* isomer.[2c,f] No unambiguous evidence for the configuration of **14** is available. However, hydrolysis of **13** furnishes (*Z*)-**15** exclusively, which testifies to the specificity of the bromine−lithium exchange reaction and to the configurational stability of the lithium carbenoid.[2b,c,e,f] Therefore, the silylated product is expected to be (*Z*)-**14**; it is configurationally stable.[2e] (*Z*)-**14** was lithiated under formation of the silyllithiophosphaalkene **16**. Surprisingly, the reaction with water at −90 °C did not furnish the expected isomerically pure *cis* hydrogen product (*E*)-**17**. Instead, a mixture of (*E*)-**17** and (*Z*)-**17**[2e] was obtained in a 1:1 ratio.

Transmetalation of the (*E*)-/(*Z*)-**16** mixture with zinc chloride or magnesium bromide furnished the *trans*-metal phosphaalkenes **18a** and **18b**, respectively; they are stable at room temperature. Unfortunately, the ^{31}P NMR spectrum showed a broad signal in the range 333−335 ppm, possibly due to the formation of aggregates (*vide infra*). The ^{1}H NMR spectrum of **18b**, however, showed sharp signals which (apart from a small amount of the hydrolysis product (*Z*)-**17**) indicated the presence of one compound only; the shielded position of the trimethylsilyl signal at $\delta(^{1}H, [D_8]THF)$ −0.48 proves the *cis* configuration of this group (*vide infra*). In contrast to **16**, hydrolysis of **18a**,**b** furnished only one isomer of the protonation product **17**; ^{31}P and ^{1}H NMR spectra of the crude mixture revealed a clean reaction to (*Z*)-**17**. Only traces of (*E*)-**17** were observed ($\delta(^{31}P) = 329$; $^{2}J(PH) = 25$). Although a mixture of isomers of **17** had been prepared before by Appel *et al.*, only indirect evidence for the configuration of (*Z*)-**17**[2e,5] was available. Our product from **18** showed a smaller $^{2}J(PH)$ coupling of 18 Hz which, according to the "*cis* rule",[5] is an indication for the *Z* configuration. Better evidence was obtained by an alternative synthesis of (*Z*)-**17**. The *cis* bromophosphaalkene (*Z*)-**15** was subjected to bromine-lithium exchange with butyllithium and followed by reaction with trimethylsilyl chloride to give (*Z*)-**17** (Scheme 5). A third empirical method for the determination of the configuration of **17** is to make use of the resonance frequency of the trimethylsilyl group in the ^{1}H NMR spectrum. In general, we find that the trimethylsilyl group at the position *cis* relative to the Mes* group is shielded compared to the *trans*-positioned trimethylsilyl group of the other isomer. This can be explained by the shielding effect of the aromatic ring of the Mes* group. From X-ray crystal structures and molecular models of phosphaalkenes, it appears that a sufficiently large *cis* substituent is indeed positioned in the shielding cone; note that, for example, the C−H bond is too short to bring its proton into the shielding cone of the Mes* group. We feel that this criterion will be helpful in similar cases of configuration assignment.

The low configurational stability of **16** is remarkable. Although the reaction of (*E*)-/(*Z*)-**16** with water at −90 °C furnished two isomers of the hydrolysis product **17**, we could not detect two independent isomeric species of **16** by low-temperature ^{31}P NMR experiments. At −93 °C, in a Trapp mixture, only one broad signal was detected at $\delta(^{31}P)$ 273, most probably indicating a rapid isomerization of (*E*)-/(*Z*)-**16** on the NMR time scale. Lowering the temperature to −113 °C did not result in any effect on this signal. In the analogous carbon series, the cis-trans isomerization of (1-lithio-1-alkenyl)trimethylsilanes has been reported.[16−19] A common observation is that, in ether and in THF, α-silyl-α-lithioalkenes of the type RHC=C(Li)$SiMe_3$ are configurationally stable at temperatures below −70 °C. At higher temperatures, mixtures of the hydrolysis products RHC=C(H)$SiMe_3$ are obtained in an *E*:*Z* ratio of 87:13 (±5%). The predominant formation of the *E* isomer is probably due to steric hindrance between the alkyl group (R) and the trimethylsilyl group. Against this background, the high configurational stability of the transmetalated products **18a**,**b** is not fully understood. Probably, the phosphorus atom plays a key role in this matter because this profound stabilizing effect is not observed in the analogous β-carbon systems. Although in 1-metallo-1-(trimethylsilyl)-1-octenes[17] the rate of the cis−trans isomerization decreases from lithium to magnesium and zinc, no isomerically pure *trans* products can be obtained after hydrolysis as found for **18a** and **18b**.

Similarly, the formation of only one *cis*-trimethylsilyl isomer of **18a** and **18b** in a strongly coordinating medium such as THF is surprising. Zweifel *et al.* reported the influence of the solvent on the isomer ratio of 1-metallo-1-(trimethylsilyl)-1-octenes in ethereal and hydrocarbon solution.[17] In diethyl ether or THF solution, an *E*:*Z* ratio of 86:14 was found in the hydrolyzed

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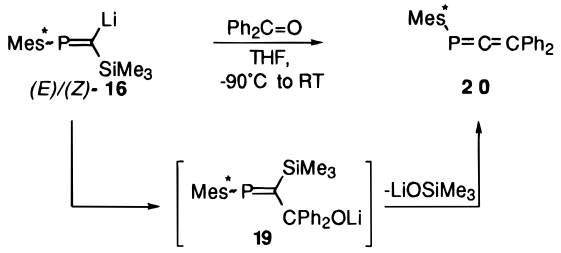
Scheme 6



products. On the other hand, in hydrocarbon solution a *E*:*Z* ratio of 10:90 was observed. This was explained by the formation of aggregates in hydrocarbon solution which favor the *trans* metal isomers. It is doubtful whether this mechanism may be extrapolated to **18a**,**b**, as these compounds were obtained in THF solution, where they are expected to be monomeric; on the other hand, the previously mentioned broad ^{31}P signal of **18b** points to an unusual bonding situation. Clearly, this matter needs further investigation.

α-(Trimethylsilyl)-α-lithiophosphaalkene (*E*)-/(*Z*)-**16** was used for a new direct synthesis of phosphaallene **20**[20,21] from **12** by the reaction sequence presented in Scheme 6. Addition of benzophenone to (*E*)-/(*Z*)-**16** furnished **20** in high yield (95%) in a Peterson olefination: 1,2-addition of (*E*)-/(*Z*)-**16** to benzophenone presumably proceeds to form **19**, which is converted to **20** with elimination of lithium trimethylsilanolate.

The conversion of **19** to **20** actually takes place below room temperature, because the ^{31}P NMR spectra of the crude reaction mixture showed complete formation of the product before hydrolysis. This behavior is in contrast to that of the analogous carbon alkenes where the intermediate alcohols can be isolated[19] before they go on to the olefin with elimination of the lithium silanolate.

Conclusion

The phosphavinylidene carbenoid **2** has proven to be a versatile reagent for the synthesis of new (phosphaalkenyl)metal compounds. Transmetalation of **2** with magnesium bromide, zinc chloride, or mercury chloride furnished carbenoids **5** and **6** with increased stability compared to **2**.

Like most normal organolithium reagents, carbenoid **2** reacted with aldehydes by a clean 1,2-addition to the carbonyl group. The magnesium carbenoid **5a** turned out to be a convenient alternative for **2**. It is more stable and has a reactivity sufficient for the 1,2-addition to carbonyl groups. In comparison to **2**, its basicity is lower, which makes it suitable for the 1,2-addition to enolizable ketones such as acetophenone, and it reacts with acetyl chloride to furnish a β-phosphaenone.

Bromine−lithium exchange between (*Z*)-**14** and *n*-butyllithium furnished the isomerically unstable 2-lithio-2-(trimethylsilyl)phosphaalkene (*E*)-/(*Z*)-**16**. While its β-carbon analogues, the 1-lithio-1-(trimethylsilyl)alkenes, are configurationally stable at temperatures below −70 °C, **16** undergoes very rapid cis−trans isomerization at −90 °C. Hydrolysis of (*E*)-/(*Z*)-**16** gave (*E*)-/(*Z*)-**17** in a 1:1 ratio. However, transmetalation of (*E*)-/(*Z*)-**16** with magnesium bromide or zinc chloride produced only (*Z*)-**18a** or (*E*)-**18b**, respectively; the reason for this is not clear at the moment. The isomer mixture of (*E*)-/(*Z*)-**16** was used for a new convenient synthesis of phosphaallene **20**[20,21] with dibromophosphaalkene **12** as the ultimate starting material.

In general, the chemistry of the metal derivatives of phosphaalkene described in this paper is analogous to that of their "carbon alkene" analogues. However, in certain cases, there is a considerable difference in the rates with which these reactions occur, for instance in the cis−trans isomerization of **16** and **18** or the Peterson elimination of **19**. The origin of these differences will be a matter for future investigations.

Experimental Section

All experiments were performed in dried glassware and under nitrogen. Solvents were distilled from sodium benzophenone (THF) or lithium aluminum hydride (pentane). All solid starting materials were dried *in vacuo*. Liquids were distilled under N_2 prior to use. A THF solution of magnesium bromide was prepared from magnesium and dibromoethane. A solution of zinc chloride was prepared by dissolving zinc chloride which had been melted *in vacuo*. Mercury dichloride was heated *in vacuo* and dissolved in THF. NMR spectra were recorded with a Bruker AC 200 spectrometer (^{1}H, ^{13}C) or with a Bruker WM 250 spectrometer (^{31}P). Tetramethylsilane (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P) was used as an external standard. High-resolution mass spectra (HRMS) were recorded with a Finnigan MAT 5 spectrometer. Elemental analyses of C, H, and O were performed by the department of microanalysis of the Rijksuniversiteit Groningen with a Heraeus CHN-O-RAPID Elemental Analyzer in combination with an IR-gas analyzer for the detection of carbon monoxide (BINOS, Leybold-Heraeus). In the case of **10** no elemental analysis was performed due to impurities. Instead, it was subjected to HRMS.

General Procedure for the Preparation of 5a,b and 6a,b. A solution of *n*-butyllithium in hexane (0.63 mL, 1.6 M, 1.0 mmol) was added dropwise to a suspension of (dichloromethylene)(2,4,6-tri-*tert*-butylphenyl)phosphane (**1**; 0.36 g, 1.0 mmol) in THF (10 mL) at −110 °C. The stirred mixture was warmed to −90 °C until a clear yellowish solution was obtained. A solution of of magnesium bromide in THF (5 mL, 0.2 M, 1.0 mmol), or zinc chloride (2 mL, 0.5 M, 1.0 mmol) was added at −90 °C. After warming of the reaction mixture to 15 °C (**5a**) or room temperature (**5b**), respectively, deuterium oxide was added. The solvent was evaporated, the residue was extracted with pentane, and the extract was filtered. Evaporation of the solvent from the filtrate furnished (*Z*)-[D]**3**. The synthesis of **6a** and **6b** was performed analogously to that of **5a** and **5b**, but only 0.5 mmol of magnesium bromide or zinc chloride was added. Workup after deuterolysis furnished a colorless powder of (*Z*)-[D]**3** (yield 0.33 g, 0.95 mmol, 95%); mp 82−84 °C. ^{1}H NMR ($CDCl_3$): δ 1.37 (s, 9H, *p*-*t*-Bu), 1.53 (s, 18H, *o*-*t*-Bu), 7.45 [d, ^4J(HP) = 1.35 Hz, 2H, Ar *H*]. ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 31.2 [s, *p*-C(CH_3)$_3$], 32.5 [d, ^4J(CP) = 6.8 Hz, *o*-C(CH_3)$_3$], 34.9 [s, *p*-*C*(CH_3)$_3$], 37.7 [s, *o*-*C*(CH_3)$_3$], 121.8 [d, ^3J(PC) = 1.2 Hz, *m*-Ar], 132.3 [d,^1J(CP) = 53.3 Hz, *ipso*-Ar], 150.6 (s, *p*-Ar), 149.2 [d, ^1J(CP) = 58.8 Hz, P=*C*], 153.6 [d, ^2J(CP) = 2.1 Hz, *o*-Ar]. ^{31}P NMR ($CDCl_3$): δ 250.

General Procedure for the Preparation of 5c and 6c. A solution of *n*-butyllithium in hexane (0.63 mL, 1.6 M, 1.0 mmol) was added dropwise to a suspension of of (dichloromethylene)(2,4,6-tri-*tert*-butylphenyl)phosphane (**1**; 0.36 g, 1.0 mmol) in THF (10 mL) at −110 °C. The stirred mixture was warmed to −90 °C until a clear yellowish solution was obtained. A solution of 1 mmol of mercury chloride in THF (5 mL, 0.2 M, 1.0 mmol) (for **5c**) or 0.5 mmol of mercury chloride

(20) Yoshifuji, M.; Toyota, K.; Shibayama, K.; Inamoto, N. *Tetrahedron Lett.* **1984**, *25*, 1809−1812.
(21) Appel, R.; Winkhaus, V.; Knoch, F. *Chem. Ber.* **1986**, *119*, 2466−2472.

in THF (2.5 mL, 0.2 M, 0.5 mmol) (for **6c**) was added at −90 °C. After warming of the reaction mixture to room temperature the solvent was evaporated, the residue was extracted with toluene, and the extract was filtered. Evaporation of the solvent from the filtrate followed by crystallization of the residue from diethyl ether/acetonitrile yielded the pure products.

***(E)*-[(Chloromercurio)chloromethylene](2,4,6-tri-*tert*-butylphenyl)phosphane (5c):** colorless crystals (yield 0.48 g, 0.86 mmol, 86%); mp 205−210 °C dec. ^{1}H NMR (C_6D_6): δ 1.32 (s, 9H, *p*-*t*-Bu), 1.53 (s, 18H, *o*-*t*-Bu), 7.57 [d, 2H, ^4J(HP) = 1.3 Hz, Ar *H*]. ^{13}C NMR ($CDCl_3$): δ 31.2 [s, *p*-C(CH_3)$_3$], 32.7 [d, ^4J(CP) = 6.5 Hz, *o*-C(CH_3)$_3$], 34.9 [s, *p*-*C*(CH_3)$_3$], 37.6 [s, *o*-*C*(CH_3)$_3$], 121.8 (s, *m*-Ar), 132.6 [d, ^1J(CP) = 66.2 Hz, *ipso*-Ar], 151.2 (s, *p*-Ar), 153.6 [d, ^2J(CP) = 2.21 Hz, *o*-Ar], 178.6 [d, ^1J(CP) = 98.1 Hz, P=*C*]. ^{31}P NMR ($CDCl_3$): δ 281 [d, ^2J(P^{199}Hg) = 1439 Hz]. MS (70 eV): *m*/*z* (%) 558 (1) [M$^+$], 323 (87) [M$^+$ − HgCl], 288 (19) [M$^+$ − HgCl − Cl]. HRMS: calcd for $C_{19}H_{29}P^{200}Hg^{35}Cl_2$ 558.1067, found 558.1063. Anal. Calcd for $C_{19}H_{29}PHgCl_2$: C, 40.76; H, 5.22; Hg, 35.82. Found: C, 40.77; H, 5.29; Hg, 35.74.

(*E*,*E*)-Mercuriobis[(chloromethylene)(2,4,6-tri-*tert*-butylphenyl)phosphane] (6c): colorless crystals (yield 0.40 g, 0.9 mmol, 90%); mp 195−196 °C. ^{1}H NMR ($CDCl_3$): δ 1.27 (s, 18H, *p*-*t*-Bu), 1.47 (s, 36H, *o*-*t*-Bu), 7.32 (s, 4H, Ar *H*). ^{13}C NMR ($CDCl_3$): δ 31.2 [s, *p*-C(CH_3)$_3$], 32.7 [d, ^4J(CP) = 3.4 Hz, *o*-C(CH_3)$_3$], 34.8 [s, *p*-*C*(CH_3)$_3$], 37.6 [s, *o*-*C*(CH_3)$_3$], 121.5 (s, *m*-Ar), 133.4 [d, ^1J(CP) = 69.0 Hz, *ipso*-Ar], 150.5 (s, *p*-Ar), 153.4 (s, *o*-Ar), 197.1 [dd, ^1J(CP) = 91.7 Hz, ^3J(CP) = 8.3 Hz, P=*C*]. ^{31}P NMR ($CDCl_3$): δ 277 [d, ^2J(P^{199}Hg) = 993 Hz]. MS (70 eV): *m*/*z* (%) 323 (100) [M$^+$ − Mes*P=CClHg], 288 (26) [M$^+$ − Mes*P=CClHg − Cl]. HRMS: calcd for $C_{38}H_{58}P_2{}^{198}Hg^{35}Cl_2$ 844.3060, found 844.3064. Anal. Calcd for $C_{38}H_{58}P_2HgCl_2$: C, 53.80; H, 6.90; Hg, 23.64. Found: C, 54.39; H, 7.23; Hg, 23.41.

General Procedure for the Preparation of 7−9. A solution of *n*-butyllithium in hexane (2.5 mL, 1.6 M, 4 mmol) was added dropwise to a suspension of (dichloromethylene)-(2,4,6-tri-*tert*-butylphenyl)phosphane (**1**; 1.44 g, 4 mmol) in THF (25 mL) at −110 °C. The stirred mixture was warmed to −90 °C until a clear yellowish solution was obtained. To this solution was added benzaldehyde (0.43 g, 4 mmol), benzophenone (0.73 g, 4 mmol), or crotonaldehyde (0.28 g, 4 mmol), respectively, at −90 °C. After the reaction mixture was warmed to room temperature for 1 h, a saturated aqueous solution of ammonium chloride was added. The solvent was evaporated, the residue was extracted with pentane, and the extract was filtered. Evaporation of the solvent from the filtrate followed by crystallization of the residue from acetonitrile (**7** and **8**) or pentane (**9**) yielded pure products.

***(Z)*-2-Chloro-2-[(2,4,6-tri-*tert*-butylphenyl)phosphanylidene]-1-phenylethanol (7):** colorless crystals (yield 1.61 g, 3.76 mmol, 94%); mp 121−123 °C. ^{1}H NMR (C_6D_6): δ 1.29 (s, 9H, *p*-*t*-Bu), 1.47 (s, 9H, *o*-*t*-Bu), 1.58 (s, 9H, *o*-*t*-Bu), 2.25 [d, 1H, ^3J(HH) = 5.3 Hz, OH], 5.59 [dd, 1H, ^3J(HH) = 5.2 Hz, ^3J(HP) = 12.7 Hz, allyl H], 7.17 [s, 2H, Ar *H*], 7.1−7.5 (m, 5H, Ph *H*). ^{13}C NMR (C_6D_6): δ 31.4 [s, *p*-C(CH_3)$_3$], 32.8 [d, ^4J(CP) = 6.8 Hz, *o*-C(CH_3)$_3$], 32.9 [d, ^4J(CP) = 7.15 Hz, *o*-C(CH_3)$_3$], 35.1 [s, *p*-*C*(CH_3)$_3$], 38.1 [s, *o*-*C*(CH_3)$_3$], 38.2 [s, *o*-*C*(CH_3)$_3$], 79.5 [d, ^2J(PC) = 37.0 Hz, *C*OH], 122.3 [s, *m*-Ar], 122.4 [s, *m*-Ar], 127.5 (s, Ph *C*), 134.2 [d, ^1J(CP) = 50.0 Hz, *ipso*-Ar], 140.8 [d, ^3J(PC) = 10.1 Hz, *ipso*-Ph *C*], 151.0 (s, *p*-Ar), 154.1 [d, ^2J(CP) = 2.6 Hz, *o*-Ar], 154.4 [d, ^2J(CP) = 2.7 Hz, *o*-Ar], 173.4 [d, ^1J(CP) = 64.7 Hz, P=*C*]. ^{31}P NMR (C_6D_6): δ 238. MS (70 eV): *m*/*z* (%) 430 (7) [M$^+$], 395 (37) [M$^+$ − Cl], 378 (10) [M$^+$ − OH − Cl]. HRMS: calcd for $C_{26}H_{36}PO^{35}Cl$ 430.2192, found 430.2192. Anal. Calcd for $C_{26}H_{36}POCl$: C, 72.45; H, 8.42; O, 3.71. Found: C, 72.35; H, 8.41; O, 3.80.

***(Z)*-2-Chloro-2-[(2,4,6-tri-*tert*-butylphenyl)phosphanylidene]-1,1-diphenylethanol (8):** slightly orange crystals (1.92 g, 3.80 mmol, 95%); mp 100−102 °C. ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 9H, *p*-*t*-Bu), 1.50 (s, 18H, *o*-*t*-Bu), 3.30 (br s, 1H, OH), 7.30−7.39 (m, 6H, Ph *H*), 7.51−7.56 (m, 4H, Ph *H*), 7.42 [d, 2H, ^4J(HP) = 1.5 Hz, Ar *H*]. ^{13}C NMR ($CDCl_3$): δ 31.2 [s, *p*-C(CH_3)$_3$], 32.8 [d, ^4J(CP) = 7.2 Hz, *o*-C(CH_3)$_3$], 34.8 [s, *p*-*C*(CH_3)$_3$], 37.8 [s, *o*-*C*(CH_3)$_3$], 85.3 [d, ^2J(PC) = 23.1 Hz, allyl *C*], 122.1 (s, *m*-Ar), 128 (m, Ph *C*), 134.7 [d, ^1J(CP) = 57.4 Hz, *ipso*-Ar], 143.7 [d, ^3J(PC) = 7.2 Hz, *ipso*-Ph *C*], 150.5 (s, *p*-Ar), 153.5 [d, ^2J(CP) = 3.0 Hz, *o*-Ar], 172.8 [d, ^1J(CP) = 71.7 Hz, P=*C*]. ^{31}P NMR ($CDCl_3$): δ 259. MS (70 eV): *m*/*z* (%) 505 (4) [M$^+$], 489 (19) [M$^+$ − OH], 471 (100) [M$^+$ − Cl]. HRMS: calcd for $C_{32}H_{40}PO^{35}Cl$ 506.2507, found 506.2505. Anal. Calcd for $C_{32}H_{40}POCl$: C, 75.79; H, 7.95; O, 3.15. Found: C, 75.71; H, 7.82; O, 3.09.

***(Z)*-5-Chloro-5-[(2,4,6-tri-*tert*-butylphenyl)phosphanylidene]-4-hydroxypent-2-ene (9):** colorless crystals (yield: 1.21 g, 3.0 mmol, 77%); mp 87−90 °C. ^{1}H NMR ($CDCl_3$): δ 1.26 (s, 9H, *p*-*t*-Bu), 1.37 (s, 9H, *o*-*t*-Bu), 1.41 (s, 9H, *o*-*t*-Bu), 1.65 [d, 3H, ^3J(HH) = 6.5 Hz, Me], 2.16 (br s, 1H, OH), 4.96 [dd, 1H, ^3J(PH) = 12.0 Hz, ^3J(HH) = 6.4 Hz, vinyl *H*], 5.56 [dd, 1H, ^3J(HH) = 15.2 Hz, ^3J(HH) = 6.4 Hz, olefinic *H*], 5.78 [dq, 1H, ^3J(HH) = 15.2 Hz, ^3J(HH) = 6.5 Hz, olefinic *H*], 7.34 [d, 2H, ^4J(HP) = 1.6 Hz, Ar *H*]. ^{13}C NMR ($CDCl_3$): δ 17.6 (s, Me), 31.2 [s, *p*-C(CH_3)$_3$], 32.44 [d, ^4J(CP) = 7.0 Hz, *o*-C(CH_3)$_3$], 32.40 [d, ^4J(CP) = 6.8 Hz, *o*-C(CH_3)$_3$], 34.9 [s, *p*-*C*(CH_3)$_3$], 37.7 [s, *o*-*C*(CH_3)$_3$], 37.8 [s, *o*-*C*(CH_3)$_3$], 77.7 [d, ^2J(PC) = 35.6 Hz, allyl *C*], 121.85 [s, *m*-Ar], 121.87 [s, *m*-Ar], 128.9 (s, olefinic *C*), 130.1 [d, ^3J(CP) = 10.8 Hz], 133.2 [d, ^1J(CP) = 52.4 Hz, *ipso*-Ar], 150.6 (s, *p*-Ar), 153.3 [d, ^2J(CP) = 2.6 Hz, *o*-Ar], 153.6 [d, ^2J(CP) = 2.5 Hz, *o*-Ar], 172.1 [d, ^1J(CP) = 63.1 Hz, P=*C*]. ^{31}P NMR ($CDCl_3$): δ 237. MS (70 eV): *m*/*z* (%) 394 (4) [M$^+$], 377 (32) [M$^+$ − OH], 359 (98) [M$^+$ − Cl]. HRMS: calcd. for $C_{23}H_{36}PO^{35}Cl$ 394.2192, found 394.2192. Anal. Calcd for $C_{23}H_{36}POCl$: C, 69.94; H, 9.19; O, 4.05. Found: C, 69.52; H, 9.37; O, 4.08.

***(Z)*-2-Chloro-2-[(2,4,6-tri-*tert*-butylphenyl)phosphanylidene]-1-methyl-1-phenylethanol (10).** A solution of *n*-butyllithium in hexane (2.5 mL, 1.6 M, 4 mmol) was added dropwise to a suspension of (dichloromethylene)(2,4,6-tri-*tert*-butylphenyl)phosphane (**1**; 1.44 g, 4 mmol) in THF (25 mL) at −110 °C. The stirred mixture was warmed to −90 °C until a clear yellowish solution was obtained. At the same temperature a solution of magnesium bromide in THF (20 mL, 0.2 M, 4.0 mmol) was added and the reaction mixture was warmed to −5 °C. At that temperature acetophenone (0.48 g, 4 mmol) was added. After the reaction mixture was warmed to room temperature for 1 h, a saturated aqueous solution of ammonium chloride was added. The solvent was evaporated, the residue was extracted with pentane, and the extract was filtered. After evaporation of the solvent from the filtrate, the products were separated by column chromatography (silica gel, 35−70 mesh). The byproduct (**3**) was collected by elution with pentane. The product was collected by elution with diethyl ether. Evaporation of the solvent furnished a yellowish oil which could not be crystallized: yellowish oil (1.24 g, 3.0 mmol, 75%). ^{1}H NMR ($CDCl_3$): δ 1.38 (s, 9H, *p*-*t*-Bu), 1.52 (s, 9H, *o*-*t*-Bu), 1.57 (s, 9H, *o*-*t*-Bu), 1.67 (s, 1H, OH), 2.05 [d, 3H, ^4J(CP) = 2.43 Hz, Me], 7.10−7.25 (m, 3H, Ph *H*), 7.49 [d, ^4J(CP) = 1.57 Hz, Ar *H*], 7.50−7.55 (m, 2H, Ph *H*). ^{13}C NMR ($CDCl_3$): δ 28.7 [d, ^3J(CP) = 14.7 Hz, Me], 31.3 [s, *p*-C(CH_3)$_3$], 32.7 [d, ^4J(CP) = 7.04 Hz, *o*-C(CH_3)$_3$], 34.9 [s, *p*-*C*(CH_3)$_3$], 37.8 [s, *o*-*C*(CH_3)$_3$], 70.6 [d, ^2J(PC) = 19.8 Hz, *C*OH], 121.9 [s, *m*-Ar], 122.0 [s, *m*-Ar], 127.5 (s, Ph *C*), 134.5 [d, ^1J(CP) = 54.4 Hz, *ipso*-Ar], 144.2 [d, ^3J(PC) = 6.7 Hz, *ipso*-Ph*C*], 150.4 (s, *p*-Ar), 153.5 [d, ^2J(CP) = 3.1 Hz, *o*-Ar], 177.3 [d, ^1J(CP) = 71.2 Hz, P=*C*]. ^{31}P NMR ($CDCl_3$): δ 238. MS (70 eV): *m*/*z* (%) 444 (1) [M$^+$], 427 (14) [M$^+$ − Me], 409 (16) [M$^+$ − Cl], 392 (29) [M$^+$ − OH − Cl]. HRMS: calcd for $C_{27}H_{38}PO^{35}Cl$ 444.2349, found 444.2350.

(*Z*)-(Acetylchloromethylene)(2,4,6-tri-*tert*-butylphenyl)-phosphane (11). Acetyl chloride (0.43 mL, 5 mmol) was added dropwise to a solution of **5a** (5 mmol) in THF at −5 °C, prepared as described above. The reaction mixture was warmed to room temperature. After the solvent was evapo-

rated, the residue was extracted with pentane and the extract filtered off. Evaporation of the solvent was followed by column chromatography on a column packed with silica gel 60. The byproduct (*Z*)-**3** was eluted with pentane. The product **11** was eluted with dichloromethane. Evaporation of the dichloromethane followed by crystallization from pentane yielded yellow crystals of pure **11** (yield 1.10 g, 3.00 mmol, 60%); mp 141−145 °C dec. ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 9H, *p*-*t*-Bu), 1.43 (s, 18H, *o*-*t*-Bu), 2.66 [d, ^4J(HP) = 3.71 Hz, 3H, CH_3], 7.44 [d, ^4J(HP) = 1.76 Hz, 2H, Ar *H*]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 26.9 [d, ^3J(PC) = 12.6 Hz, CH_3], δ 31.1 [s, *p*-C(CH_3)$_3$], 32.7 [d, ^4J(CP) = 6.8 Hz, *o*-C(CH_3)$_3$], 34.9 [s, *p*-*C*(CH_3)$_3$], 37.7 [s, *o*-*C*(CH_3)$_3$], 122.5 [d, ^3J(PC) = 1.2 Hz, *m*-Ar], 132.1 [d, ^1J(CP) = 53.5 Hz, *ipso*-Ar], 151.7 (s, *p*-Ar), 152.9 [d, ^2J(CP) = 2.7 Hz, *o*-Ar], 166.0 [d, ^1J(CP) = 71.6 Hz, P=*C*], 192.1 [d, ^2J(CP) = 31.4 Hz, *C*=O]. ^{31}P NMR ($CDCl_3$): δ 328. IR (KBr): $\tilde{\nu}$ 1667 cm^{-1} (C=O). HRMS: probably due to the instability of **11**, a molecular ion could not be observed and therefore no exact mass is available. For the same reason, the elemental analysis was not quite satisfactory. Anal. Calcd for $C_{21}H_{32}POCl$: C, 68.74; H, 8.79; O, 4.36. Found: C, 67.50; H, 8.94; O, 5.22.

(Dibromomethylene)(2,4,6-tri-*tert*-butylphenyl)phosphane (12). A solution of *n*-butyllithium in hexane (43 mL, 1.6 M, 68 mmol) was added dropwise to a solution of a mixture of dichloro(2,4,6-tri-*tert*-butylphenyl)phosphane (12.1 g, 34 mmol) and tetrabromomethane (11.3 g, 34 mmol) in THF (300 mL) at −110 °C. The stirred mixture was slowly warmed to room temperature. After the solvent was evaporated, the residue was extracted with pentane and the extract filtered off. Evaporation of the solvent from the filtrate followed by crystallization of the residue from pentane yielded colorless crystals of pure **12** (14.1 g, 31.6 mmol, 93%); mp 157−158 °C (158−159 °C[2c]). ^{1}H NMR (C_6D_6): δ 1.28 (s, 9H, *p*-*t*-Bu), 1.49 (s, 18H, *o*-*t*-Bu), 7.52 [d, ^4J(HP) = 1.6 Hz, 2H, Ar *H*]. ^{13}C NMR (C_6D_6): δ 31.4 [s, *p*-C(CH_3)$_3$], 32.9 [d, ^4J(CP) = 7.0 Hz, *o*-C(CH_3)$_3$], 35.2 [s, *p*-*C*(CH_3)$_3$], 38.0 [s, *o*-*C*(CH_3)$_3$], 122.8 (s, *m*-Ar), 128.0 [d, ^1J(CP) = 86.8 Hz, P=*C*], 139.7 [d, ^1J(CP) = 57.0 Hz, *ipso*-Ar], 152.1 (s, *p*-Ar), 153.5 [d, ^2J(CP) = 2.5 Hz, *o*-Ar]. ^{31}P NMR (C_6D_6): δ 271. Spectra were identical with those reported.[2c,4d]

(*Z*)-[Bromo(trimethylsilyl)methylene](2,4,6-tri-*tert*-butylphenyl)phosphane ((*Z*)-14). A solution of *n*-butyllithium in hexane (8.9 mL, 1.6 M, 14.2 mmol) was added dropwise to a solution of a mixture of **12** (6.4 g, 14.2 mmol) in 150 mL of Trapp mixture (60 mL of THF, 60 of mL diethyl ether, 30 mL of pentane) at −130 °C. The stirred mixture was warmed to −100 °C, and chlorotrimethylsilane (1.54 g, 14.2 mmol) was added. With stirring, the mixture was warmed to room temperature. After evaporation of the solvent, the residue was extracted with pentane and the extract filtered. Evaporation of the solvent from the filtrate followed by crystallization of the residue from pentane yielded 90% of **14** with 98% isomeric purity: slightly yellowish crystals (yield 5.6 g, 12.8 mmol, 90%); mp 92−95 °C (106 °C[2c]). ^{1}H NMR ($CDCl_3$): δ 0.30 [d, ^4J(PC) = 1.05 Hz, 9H, Si(CH_3)$_3$], 1.35 (s, 9H, *p*-*t*-Bu), 1.48 (s, 18H, *o*-*t*-Bu), 7.40 [d, ^4J(PH) = 1.26 Hz, 2H, Ar *H*]. ^{13}C NMR ($CDCl_3$): δ −0.70 [d, ^3J(PC) = 8.8 Hz, Si(CH_3)$_3$], 31.4 [s, *p*-C(CH_3)$_3$], 33.0 [d, ^4J(CP) = 7.1 Hz, *o*-C(CH_3)$_3$], 35.0 [s, *p*-*C*(CH_3)$_3$], 37.7 [s, *o*-*C*(CH_3)$_3$], 121.8 (s, *m*-Ar), 140.3 [d, ^1J(CP) = 53.3 Hz, *ipso*-Ar], 150.3 (s, *p*-Ar), 152.4 [d, ^2J(CP) = 2.1 Hz, *o*-Ar], 167.9 [d, ^1J(CP) = 78.1 Hz, P=*C*]. ^{31}P NMR ($CDCl_3$): δ 302. Spectra were identical with those reported.[2e]

General Procedure for the Synthesis of (*E*)-/(*Z*)-16, (*Z*)-18a, (*E*)-18b, and (*Z*)-17. A solution of *n*-butyllithium in hexane (0.32 mL, 1.6 M, 0.5 mmol) was added dropwise to a solution of (*Z*)-**14** (0.22 g, 0.5 mmol) in THF (5 mL) at −90 °C, furnishing a solution of (*E*)/(*Z*)-**16**. To the deep orange solution was added respectively a solution of magnesium bromide (2.5 mL, 0.2 M, 0.5 mmol) or zinc chloride (1 mL, 0.5 M, 0.5 mmol), furnishing a solution of (*Z*)-**18a** or (*E*)-**18b**. The stirred mixture was warmed to room temperature.

For the determination of the configuration of the transmetalation products, at room temperature, a saturated aqueous solution of ammonium chloride was added. After evaporation of the solvent, water and pentane were added. Extraction of the organic products with pentane and evaporation of the pentane and other volatile products furnished a colorless powder of (*Z*)-**17** (yield 0.17 g, 0.48 mmol, 95%). ^{1}H NMR ($CDCl_3$): δ −0.37 [s, 9H, Si(CH_3)$_3$], 1.34 (s, 9H, *p*-*t*-Bu), 1.55 (s, 18H, *o*-*t*-Bu), 7.36 [d, ^4J(PH) = 1.1 Hz, 2H, Ar *H*], 7.78 [d, ^2J(PH) = 17.9 Hz, 1H, P=C*H*]. ^{13}C NMR ($CDCl_3$): δ −1.43 [d, ^3J(PC) = 3.32 Hz, Si(CH_3)$_3$], 31.6 [s, *p*-C(CH_3)$_3$], 33.6 [d, ^4J(CP) = 8.20 Hz, *o*-C(CH_3)$_3$], 34.8 [s, *p*-*C*(CH_3)$_3$], 38.1 [s, *o*-*C*(CH_3)$_3$], 121.4 (s, *m*-Ar), 141.2 [d, ^1J(CP) = 66.8 Hz, *ipso*-Ar], 149.9 (s, *p*-Ar), 153.3 [d, ^2J(CP) = 1.66 Hz, *o*-Ar], 173.0 [d, ^1J(CP) = 53.6 Hz, P=*C*]. ^{31}P NMR ($CDCl_3$): δ 335. Spectra were identical with those reported.[2c]

2-[(2,4,6-tri-*tert*-butylphenyl)phosphanylidene]-1,1-diphenylethene (20). A solution of *n*-butyllithium in hexane (0.94 mL, 1.6 M, 1.5 mmol) was added dropwise to a solution of (*Z*)-**14** (0.66 g, 1.5 mmol) in THF (15 mL) at −110 °C. To the deep orange solution was added benzophenone (0.27 g, 1.5 mmol). After the stirred solution was warmed to room temperature, a saturated aqueous solution of ammonium chloride was added. After evaporation of the solvent, water and pentane were added. The organic products were extracted with pentane. Crystallization from pentane furnished colorless crystals of **20** (yield 0.64 g, 1.43 mmol, 95%); mp 152−155 °C (160−161.5 °C[19]). ^{1}H NMR ($CDCl_3$): δ 1.38 (s, 9H, *p*-*t*-Bu), 1.56 (s, 18H, *o*-*t*-Bu), 7.31 (s, 10H, Ph *H*), 7.45 [d, 2H, ^4J(HP) = 1.7 Hz, Ar *H*]. ^{13}C NMR ($CDCl_3$): δ 31.3 [s, *p*-C(CH_3)$_3$], 33.4 [d, ^4J(CP) = 7.2 Hz, *o*-C(CH_3)$_3$], 34.8 [s, *p*-*C*(CH_3)$_3$], 38.1 [s, *o*-*C*(CH_3)$_3$], 122.0 (s, *m*-Ar), 136.2 [d, ^1J(CP) = 10.2 Hz, *ipso*-Ar], 149.6 (s, *p*-Ar), 154.2 [d, ^2J(CP) = 3.6 Hz, *o*-Ar], 128.3 [d, ^2J(CP) = 6.4 Hz, P=C=*C*], 237.6 [d, ^1J(CP) = 26.6 Hz, P=*C*]. ^{31}P NMR ($CDCl_3$): δ 72.7. MS (70 eV): *m*/*z* (%) 454 (40) [M$^+$], 397 (100) [M$^+$ − *t*-Bu]. HRMS: calcd for $C_{32}H_{39}P$ 454.2789, found 454.2789. Spectra were identical with those reported in the literature.[19]

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