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# Palladium(0) mediated coupling of bromophosphaalkenes with Grignard reagents [1]

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**Abstract**

Attempts to subject the phosphaalkene Mes* P = $CBr_2$ (**1**) (Mes* = supermesityl = 2,4,6-tri-*tert*-butylphenyl) to a palladium(0) catalyzed Stille-type coupling reaction with phenylmagnesium chloride failed due to elimination of palladium bromide and rearrangement to the phosphaacetylene Mes* C≡P (**2**). To prevent this undesired reaction, the monobromophosphaalkene Mes* P=C(H)Br (**6**) was used. Although both isomers are known, a new method for the synthesis of (*E*)-Mes* P=C(H)Br ((*E*)-**6**) has been developed and the compound tested in Stille-type coupling reactions with organometallic reagents. Best results were obtained in combination with Grignard reagents; aromatic, olefinic and alkynyl groups could be introduced. Most unexpected was the result when (*Z*)-Mes* P=C(Br)H ((*Z*)-**6**) was subjected to this coupling reaction: in all cases, isomerization occurred to give (*E*)-Mes* P=C(H)R (**7–17**) in high yield and purity. This method offers a convenient access to a variety of new functionalized phosphaalkenes with potentially interesting coordinating properties. The mechanism of the coupling reaction appears not to involve the usual oxidative addition step, assumed to occur in the normal Stille coupling. Attempts to elucidate the mechanism are reported and the $\eta^2$-palladium complex **19** has been tentatively identified as an intermediate.

*Keywords:* Bromophosphaalkene; Stille-coupling; Grignard reagent; Phosphaalkenes; Palladium catalysis

## 1. Introduction

Since phosphaalkenes were first reported, considerable progress has been made in developing synthetic procedures leading to functionalized phosphaalkenes [1]. A large variety of phosphaalkenes RP=CR′R″ can be prepared by introducing a P=C double bond by a Peterson-type olefination of the corresponding carbonyl compound O=CR′R″, or by a β-elimination reaction from appropriate precursors RP(Cl)–CHR′R″ which, however, must be prepared separately. Mixtures of the two *E*,*Z*-isomers are usually obtained and have to be separated by chromatographic methods. A configurationally selective introduction of new functionalities by C–C bond formation using halophosphaalkenes of a defined configuration would be desirable.

Since 1981, various methods for the synthesis of halogen substituted phosphaalkenes of the type Mes* P=$CHal_2$ (Mes* = supermesityl = 2,4,6-tri-*tert*-butylphenyl; Hal = Cl, Br, I) have been developed [2–6]. These phosphaalkenes can be regarded as convenient synthons for the preparation of functionalized phosphaalkenes. However, this has in fact only been realized in a few cases [2a,c,5–8]. Recently, our group [8], and simultaneously that of Yoshifuji [6c,d], showed that phosphavinylidene carbenoids can easily be converted to new, isomerically pure phosphaalkenes by reaction with reactive electrophiles. By this method β-phosphaenones, β-phosphaallylic alcohols, and a β-phosphaacrylic acid have been synthesized. A number of

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functionalities can be introduced, but the functionalization is limited to direct substitution reactions and excludes the introduction of olefinic and arylic groups, which are usually the product of transition metal mediated coupling reactions.

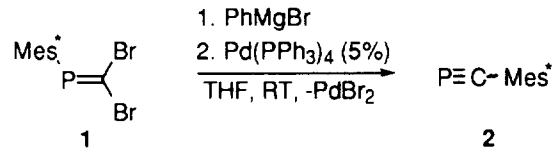
The groups of Jouaiti, [9] Yoshifuji, [10] and Mathey [11] have isolated interesting new phosphaalkene- or phosphinine-based ligand systems, indicating the great interest in systems of this type which can have unique coordinating properties. However, a general method for the synthesis of these systems from easily available phosphaalkenes does not exist. Mathey showed that 2-bromophosphinines can be functionalized by a palladium catalyzed Stille reaction with organotin reagents [11]. In the case of dihalogen-substituted phosphaalkenes this reaction fails due to elimination of palladium dihalide from the intermediate oxidative addition product [12]. We explored the possible palladium mediated functionalization of monohalophosphaalkenes using aromatic and olefinic organometallic reagents. A number of the resulting functionalized 1-phosphastyrenes have already been reported, but in most cases the required reaction conditions are vigorous and a mixture of isomers is obtained in low yield [2e,13]. Although methods for the preparation of bromomethylene-(2,4,6-tri-*tert*-butylphenyl)-phosphane are known, only the (*Z*)-isomer can easily be prepared in pure form by hydrolysis of (*Z*)-Mes*P=C(Li)Br [2c]. The (*E*)-isomer was obtained only after chromatographic separation of a mixture of isomers [2b] which is obtained by a β-elimination reaction of Mes*PH–$CHBr_2$. This is clearly inconvenient for large scale preparations.

In this publication we present a convenient synthetic procedure for the preparation of (*E*)-Mes*P=CHBr. Both isomers of (*E*)- and (*Z*)-Mes*P=CHBr were coupled with Grignard reagents by a Stille-type reaction, catalyzed by palladium(0). Using this method, olefinic, arylic and alkynyl functionalities have been introduced leading to new isomerically pure (*E*)-phosphaalkenes in high yield.

## 2. Results and discussion

### 2.1. Syntheses

Recent developments in the field of palladium(0) and platinum(0) insertion reactions into the carbon–halogen bond of halophosphinines [11] and dihalophosphaalkenes [12] document the great interest in the functionalization of these $\lambda^3\sigma^2$-heteroatom species. Our progress in developing methodologies for the direct functionalization of phosphaalkenes via phosphavinylidene carbenoids has so far been limited to reactions with $sp^3$ carbon centers and carbonyl species as electrophiles [8]. For the introduction of an $sp^2$ (aryl, alkenyl) or sp (alkynyl) functionality we studied Stille-type coupling reactions of halophosphaalkenes with organometallic reagents. In our first attempt to achieve a palladium catalyzed coupling reaction, a catalytic amount (5 mol%) of a solution of tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$), generated by dissolving a mixture of tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) and triphenylphosphine in THF, was added to a mixture of dibromophosphaalkene **1** and phenylmagnesium bromide in THF at room temperature. By means of $^{31}P$ NMR spectroscopy, only the phosphaacetylene **2** and starting material (phosphaalkene **1**) could be detected. Apparently, as described previously [12], the oxidative addition product rapidly rearranges to **2** in a process involving elimination of palladium dibromide and loss of the catalyst. This experiment proved that the rearrangement to **2** occurs at a much higher rate compared with the expected coupling reaction of **1** with phenylmagnesium bromide (Scheme 1).

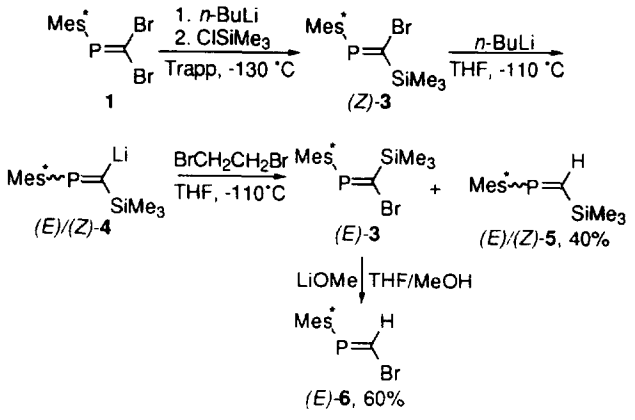



1 2

Scheme 1.

To circumvent this problem of the elimination reaction, we decided to investigate reactions with monobromophosphaalkenes. Although (*Z*)-bromophosphaalkene can easily be obtained, this phosphaalkene seemed not to be suited for the synthesis of (*E*)-functionalized phosphaalkenes; only the (*Z*)-coupling products were expected to be formed, as for the comparable monobromostyrenes, the analogous coupling reaction occurs with a high degree of retention of configuration [14]. The *Z*-isomers would be unsuitable for application as small bidentate ligands because the Lewis-base functionality in the *Z*-group and the phosphorus lone pair would be trans. For the synthesis of (*E*)-functionalized phosphaalkenes, we were convinced that an (*E*)-bromophosphaalkene was needed. The group of Appel has described methods for the synthesis of (*E*)-monobromophosphaalkene [2b–e]. However, the desired isomer can only be isolated after chromatographic separation of the two isomers which were formed. Therefore, we developed a new, convenient method for the synthesis of (*E*)-bromophosphaalkene.

The synthesis of (*E*)-bromophosphaalkene (*E*)-**6** is based on the previously described rapid isomerization of 2-lithio-2-trimethylsilylphosphaalkene (*E/Z*)-**4**. Compound **1** was converted to (*Z*)-**3** [2c], which was converted to (*E/Z*)-**4** by lithiation with *n*-butyllithium at −110°C in THF solution (Scheme 2) [8b]. To our surprise, the addition of 1,2-dibromoethane (DBE) to




Scheme 2.

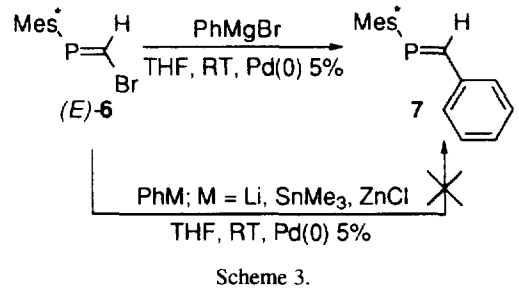
(*E*/*Z*)-**4** furnished the brominated species (*E*)-**3** (60%) as the only isomer. By this method, an overall isomerization of (*Z*)-**3** to (*E*)-**3** was accomplished; (*E*)-**3** was characterized by NMR spectroscopy and the data were found to be identical with those published [2e]. In addition to (*E*)-**3**, a substantial amount (40%) of (*E*)/(*Z*)-**5** was found in an *E*:*Z* ratio of 1:3. The origin of (*E*)/(*Z*)-**5** is not clear. This by-product was found under anhydrous conditions and is therefore not the product of the hydrolysis of (*E*)/(*Z*)-**4**; alternatively, **4** might abstract HBr from DBE, but this observation was not further investigated. Dibromoethane has proved to be the preferred halogenating reagent in this reaction. Changing the reaction conditions by varying the temperature of addition of dibromoethane, or changing the rate of warming the reaction mixture to room temperature, did not improve the yield of (*E*)-**6**. Other brominating reagents furnished mixtures of the isomers of **6**. For preparative purposes, (*E*)-**3** was not separated from (*E*)/(*Z*)-**5** but was transformed to (*E*)-**6** within 1 h by addition of a solution of lithium methoxide in methanol at room temperature. Compound (*E*)/(*Z*)-**5** remained unchanged and was separated from the desired product (*E*)-**6** by crystallization of the latter from pentane as white crystals and in 100% isomeric purity.

The reactivity of (*E*)-**6** was tested in a Stille-type coupling reaction by stirring a THF solution with phenyllithium, phenylzinc chloride, phenyltrimethyl stannane, or phenylmagnesium bromide in the presence of a catalytic amount (5%) of $Pd(PPh_3)_4$, prepared as mentioned above. The lithium, zinc, and tin reagents proved unreactive; phenylphosphaalkene (*E*)-**7** was not formed. Changing the solvent from THF to toluene, and heating the reaction mixture showed no effect. Surprisingly, (*E*)-**7** was selectively formed within 3–4 h at room temperature and in high yield (91%) when phenylmagnesium bromide was used in THF solution; it was formed with complete retention of configuration, and was isolated in 100% isomeric purity (Scheme 3). The analogous reaction in the absence of 5% of $Pd(PPh_3)_4$ gave no coupling product.

After this successful test reaction, a variety of aryl Grignard reagents, bearing electron donating and electron withdrawing substituents, was reacted (Table 1). In all cases, the coupling product (*E*)-Mes*P=C(H)R **7**–**17** was obtained in high yield (80–90%) and isomeric purity (100% (*E*)-product), except for compound **16** where the yield was 48%. Neither the electronic character of the substituent, nor the position of the substituent at the aromatic ring showed a large effect on the rate of the reaction. In all cases the reaction consumed two equivalents of Grignard reagent; the addition of one equivalent of Grignard reagent furnished mixtures containing unreacted (*E*)-**6** and the product in a 1:1 ratio (vide infra).

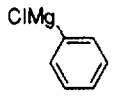
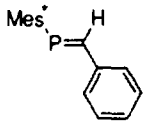
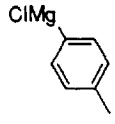
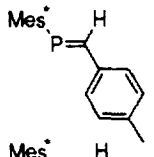
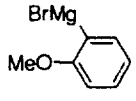
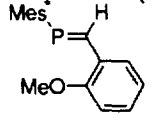
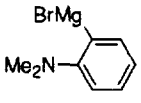
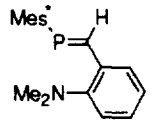
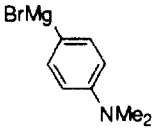
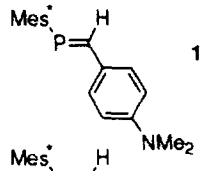
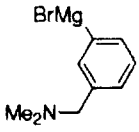
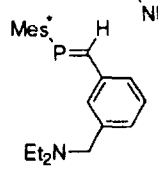
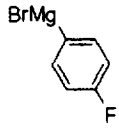
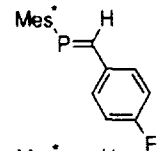
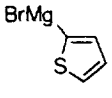
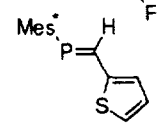
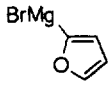
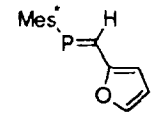
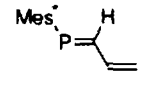
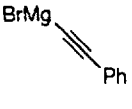
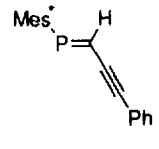
The scope of the reaction is not limited to the introduction of aromatic substituents: the addition of vinylmagnesium chloride or phenylacetylenemagnesium bromide furnished a 1-phosphabutadiene **16** (entry 15), or a phosphaenyn **17** (entry 17) respectively. The reaction with vinylmagnesium chloride gave the lowest yield (48%). After complete conversion of (*E*)-**6**, the $^{31}P$ NMR spectrum of the crude reaction mixture showed only one signal for the product **16**. The reason for the low yield is probably the instability of **16** which tends to polymerize; at room temperature the crystals of **16** gave an oil which showed no $^{31}P$ NMR absorptions. However, **16** could be characterized by NMR spectroscopy and high resolution mass spectrometry (HRMS).

The configuration of the coupling products was assigned to be trans in all cases. All products show a $^2J(HP)$ value in the range of 23.0–25.7 Hz which, according to the cis-rule, is characteristic for an (*E*)-configuration [2,5,13a]. A second characteristic feature of the (*E*)-configuration is the chemical shift of the vinylic proton signal in the $^1H$ NMR spectrum. In all cases this signal is found at 7.41–8.33 ppm. Romanenko et al. showed that there is a substantial difference between the chemical shifts of the vinylic protons of the (*E*)- and (*Z*)-isomers of phosphaalkenes of the type Mes*P=C(H)Ar. The isomer with the smaller $^2J(HP)$ coupling of approximately 25 Hz ((*E*)-isomer) shows a deshielded chemical shift in the range 8–8.6 ppm, whereas the isomer with the greater coupling $^2J(HP)$ = 45 Hz ((*Z*)-isomer) shows an upfield chemical shift of




Scheme 3.

Table 1

| Entry | RMgX | Phosphaalkene (*E*)- or (*Z*)-**6** | Conditions [a] (temp. (°C)/time (h)) | Product | | Yield (%) |
|---|---|---|---|---|---|---|
| 1 |  | *Z* | RT/3–4 |  | **7** | 90 |
| 2 | | *E* | RT/3–4 | | | 91 |
| 3 |  | *Z* | RT/3–4 |  | **8** | 90 |
| 4 |  | *Z* | 60/4–5 |  | **9** | 60 |
| 5 | | *E* | RT/4–5 | | | 84 |
| 6 |  | *Z* | 60/4–5 |  | **10** | 55 [b] |
| | | *E* | RT/4–5 | | | – [b] |
| 7 |  | *Z* | RT/4–5 |  | **11** | 90 |
| 8 | | *E* | RT/4–5 | | | 90 |
| 9 |  | *Z* | 50/3 |  | **12** | 90 |
| 10 |  | *Z* | RT/3–4 |  | **13** | 90 |
| 11 | | *E* | RT/3–4 | | | 90 |
| 12 |  | *Z* | RT/4–5 |  | **14** | 89 |
| 13 |  | *Z* | RT/4–5 |  | **15** | 89 |
| 14 | | *Z* | RT/4–5 |  | **16** | 43 |
| 15 | | *E* | RT/4–5 | | | 48 |
| 16 |  | *Z* | RT/3–4 |  | **17** | 88 |
| 17 | | *E* | RT/3–4 | | | 87 |

[a] RT, room temperature. [b] Not determined.

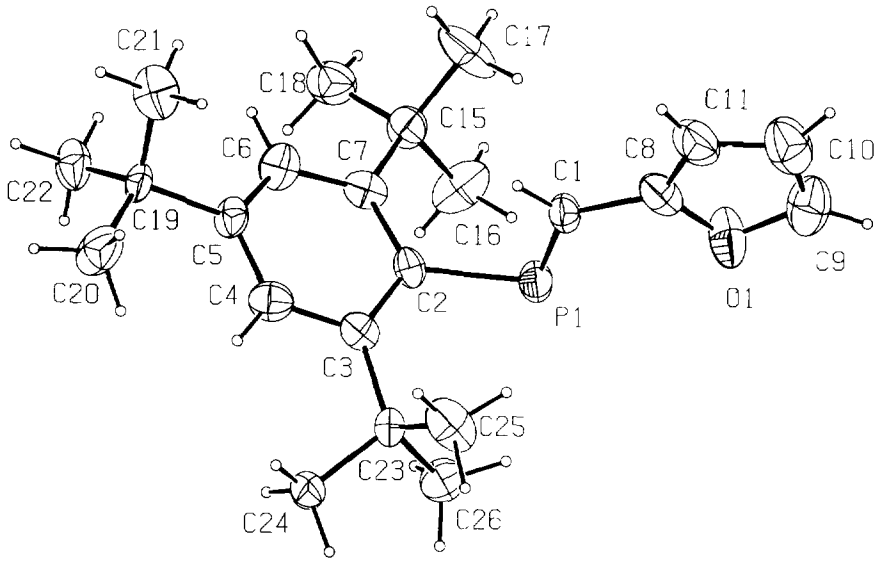



Fig. 1. Thermal motion ellipsoid presentation (50% probability level) of $C_{23}H_{33}OP$ ((*E*)-**15**).

7–7.8 ppm [13a]. X-ray structures and molecular models indicate that the hydrogen atom in the (*E*)-isomer is positioned near, but outside, the shielding cone of the aromatic supermesityl ring [2e,13c]. This causes a downfield shift of this proton signal compared with that of the (*Z*)-isomer. Again, the effect of the shielding cone of the aromatic ring of the supermesityl group on the chemical shift of substituents attached to the carbon center of the P=C double bond has been shown to be a useful tool for the assignment of the configuration of this type of phosphaalkene [8b]. In combination with the $^2J$(HP) value (cis rule) [5], the configuration of the phosphaalkene can be assigned to be trans with a high degree of certainty.

In addition, the (*E*)-configuration of one of the functionalized phosphaalkenes was unambiguously established by obtaining the crystal structure of **15** (Fig. 1, Table 2). The structure shows a furyl group positioned

Table 2
Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for (*E*)-**15**

| Atom | *x* | *y* | *z* | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| P(1) | 0.2552(4) | 0.7176(4) | 0.0731(2) | 0.0352(12) |
| O(1) | 0.1044(13) | 0.9215(13) | −0.0252(5) | 0.058(4) |
| C(1) | 0.3317(15) | 0.7986(13) | 0.0299(5) | 0.030(4) |
| C(2) | 0.4242(15) | 0.6169(13) | 0.1176(5) | 0.028(4) |
| C(3) | 0.4423(15) | 0.4834(13) | 0.1013(5) | 0.029(4) |
| C(4) | 0.5922(16) | 0.4300(15) | 0.1244(6) | 0.038(4) |
| C(5) | 0.7141(14) | 0.5001(14) | 0.1647(6) | 0.031(4) |
| C(6) | 0.6795(16) | 0.6204(16) | 0.1860(6) | 0.038(4) |
| C(7) | 0.5376(16) | 0.6802(13) | 0.1670(5) | 0.030(4) |
| C(8) | 0.2493(19) | 0.8990(14) | −0.0160(6) | 0.040(5) |
| C(9) | 0.059(2) | 1.021(2) | −0.0695(7) | 0.057(6) |
| C(10) | 0.175(2) | 1.0538(19) | −0.0846(8) | 0.061(6) |
| C(11) | 0.291(2) | 0.9725(16) | −0.0528(6) | 0.054(5) |
| C(15) | 0.5156(16) | 0.8117(14) | 0.1985(6) | 0.037(4) |
| C(16) | 0.3579(17) | 0.811(2) | 0.2037(7) | 0.056(6) |
| C(17) | 0.538(3) | 0.9439(16) | 0.1704(8) | 0.067(7) |
| C(18) | 0.6252(18) | 0.8112(16) | 0.2613(7) | 0.049(5) |
| C(19) | 0.8794(14) | 0.4458(14) | 0.1849(6) | 0.033(4) |
| C(20) | 0.8881(18) | 0.3112(18) | 0.1551(8) | 0.057(6) |
| C(21) | 0.9740(18) | 0.5522(17) | 0.1676(7) | 0.046(5) |
| C(22) | 0.9403(16) | 0.4292(17) | 0.2497(6) | 0.043(5) |
| C(23) | 0.3210(15) | 0.3898(14) | 0.0592(6) | 0.033(4) |
| C(24) | 0.3665(17) | 0.2363(14) | 0.0677(7) | 0.042(4) |
| C(25) | 0.291(2) | 0.4243(16) | −0.0048(6) | 0.055(6) |
| C(26) | 0.1675(16) | 0.3984(17) | 0.0693(7) | 0.044(5) |

$U_{eq}$ is one-third of the trace of the orthogonalized *U* tensor.

trans to the Mes*-group, with an s-*cis* configuration around the C1–C8 axis. The hydrogen atom at the phosphaalkene moiety is positioned outside the shielding cone of the aromatic Mes*-group, which accounts for the deshielding of the $^1$H NMR signal.

In order to extend this method of functionalization, we attempted to synthesize the configurationally pure (*Z*)-isomers of **7–17** by performing the analogous reaction with (*Z*)-bromophosphaalkene (*Z*)-**6**. We expected to find almost complete retention of configuration; however, surprisingly, complete inversion of configuration occurred, and only the (*E*)-isomers of **7–17** were isolated (Table 1).

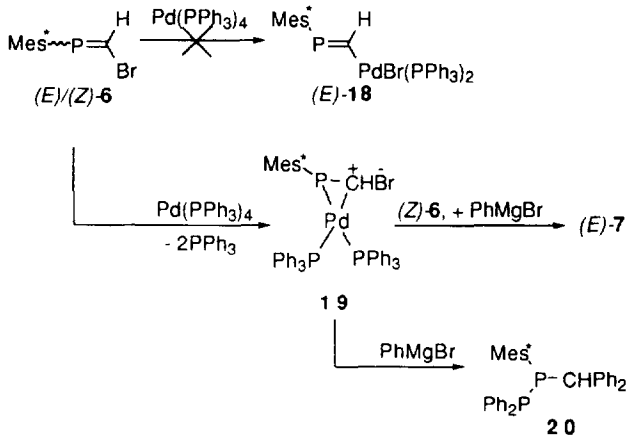
Although the (*E*)-product was isolated in good yields in most cases, aryl Grignard reagents with ortho substituents (entries 4 and 6) reacted slowly and the desired product was only formed in low yield. Stirring the reaction mixture (entry 4) for an extended period of time (20 h) at room temperature did not produce more than 20% of the coupling product. Heating the reaction mixture for 4–5 h at 60°C led to 60% conversion of (*Z*)-**6** to (*E*)-**9**. Steric hindrance seems to be an important rate determining factor when (*Z*)-**6** is used instead of (*E*)-**6**, whereas the electronic properties of the substituent on the aromatic ring of the Grignard reagent seem to be unimportant (entry 1 vs. 10).

### 2.2. Mechanistic studies

Obviously an unusual, rapid isomerization occurs during this palladium catalyzed coupling reaction. The cis–trans isomerization could occur during the coupling reaction or afterwards. The latter possibility can be excluded since it has been shown that irradiation or elevated temperatures (140°C) are needed for isomerization of the (*Z*)-isomer to the (*E*)-product. The reaction conditions used in our procedure are not vigorous enough for such an isomerization [13a–c].

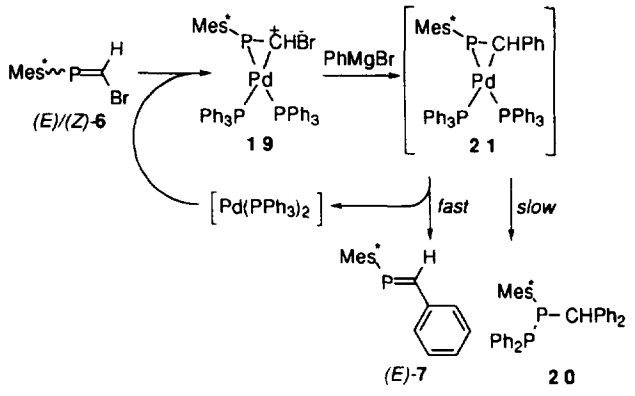
To eliminate the possibility of a palladium catalyzed isomerization of (*Z*)-**7–17** to (*E*)-**7–17**, a mixture of (*Z*)-**7** and (*E*)-**7** in a ratio of 1 : 2 (see Section 4) was reacted with a catalytic amount (5%) of $Pd(PPh_3)_4$ in THF solution. Analysis of the reaction mixture with $^{31}$P NMR spectroscopy after 4 h of stirring at room temperature showed no isomerization. Analogously, (*Z*)-**6** could isomerize to (*E*)-**6**, which in turn could react to (*E*)-**7**. Again, the addition of $Pd(PPh_3)_4$ (5%) to (*Z*)-**6** in THF solution showed no isomerization to (*E*)-**6** after 4 h of stirring at ambient temperature.

As the primary oxidative addition product of the type (*E*)-**18** is a generally accepted intermediate in palladium catalyzed reactions, we expected this species to be one of the key intermediates in the present coupling reaction. We attempted to isolate this oxidative addition product in order to obtain more information about the mechanism of the coupling reaction (Scheme 4).

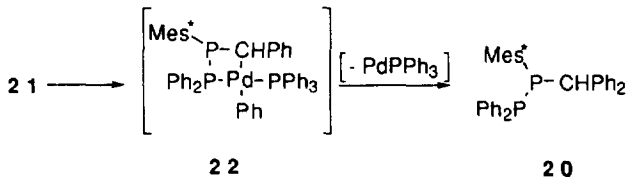



Scheme 4.

A stoichiometric amount of (*Z*)-**6** or (*E*)-**6**, respectively, was mixed with $Pd(PPh_3)_4$ in THF solution at room temperature. After 15 min of stirring, a yellow product precipitated and was studied by $^{31}$P NMR spectroscopy. To our surprise, in both cases, no $^{31}$P NMR signal compatible with the presence of (*E*)-**18** was observed; it was expected to fall in the characteristic phosphaalkene range of $\delta = 200–350$ ppm. Identical phosphorus signals were found in both cases for a compound with three different phosphorus nuclei and, additionally, of free triphenylphosphine, in a molar ratio of 1 : 2. The precipitate was isolated by evaporation of the solvent and washing the solid residue with pentane. The yellow product showed three signals at $\delta(^{31}P\{^1H\}, CDCl_3) = 64.8$ (dd, $J(PP) = 104.8$ Hz, $J(PP) = 8.1$ Hz), 24.5 (dd, $J(PP) = 8.1$ Hz, $J(PP) = 6.7$ Hz), and 21.9 (dd, $J(PP) = 104.8$ Hz, $J(PP) = 6.7$ Hz). We suggest the product to be compound **19** (Scheme 4). In the $^1$H NMR spectrum of **19**, a signal at $\delta(^1H, CDCl_3) = 2.7$ (dd, $J(HP) = 8.5$ Hz, $J(HP) = 2.1$ Hz) is assigned to proton of the C*H*Br-group which finally appears at the cis position in the product phosphaalkene. The proton coupled $^{31}$P NMR spectrum of **19** shows broad signals at 24.5 ppm and 21.9 ppm, which are assigned to the triphenylphosphine ligands. The signal at 64.8 ppm is assigned to the phosphorus originating from the phosphaalkene; it remains sharp and shows no additional coupling. An observable coupling is only found between the proton of the CHBr-group and the phosphorus of the triphenylphosphine ligands. We have not been able to isolate the product in pure form due to the presence of small amounts of triphenylphosphine oxide. Although the observed phosphorus spectrum is in accordance with structure **19**, it should be noted that Van der Knaap and coworkers have described $\eta^2$-coordinated platinum and nickel complexes of phosphaalkenes [15] and have found that the chemical shift of the phosphorus center originating from the phosphaalkene absorbs at $-34$ ppm and $-16$ ppm respectively. Our




Scheme 5.




Scheme 6.

palladium complex shows a signal at much lower field (64.8 ppm). An explanation for this relative deshielding might be associated with some cationic character at the CHBr carbon center, possibly by the contribution of an ion pair canonical structure which might also explain the rapid isomerization of **19** from either (*E*)- or (*Z*)-**6** to furnish the sterically favorable isomer of **19** with the supermesityl group and bromine trans to each other. Such ion pair character has been proposed for complexes of platinum with electron poor haloolefins [16].

Complex **19** turned out to be catalytically active. A catalytic amount of **19** was added to a mixture of (*Z*)-**6** and phenylmagnesium bromide in THF at room temperature. Within 4 h the reaction was complete and (*E*)-**7** was isolated in 90% yield (Scheme 4). Surprisingly, the addition of two equivalents of phenylmagnesium bromide to **19** in the absence of (*E*)-**6** did not furnish the coupling product (*E*)-**7**. Instead, a new set of double doublets was detected in the $^{31}$P NMR spectrum of the crude reaction mixture ($\delta(^{31}P\{^{1}H\}) = 25$ (d, $J(PP) = 201$ Hz); $-29$ (d, $J(PP) = 201$ Hz). Based on HRMS, and on the fragmentation pattern, the compound was identified as **20** (Scheme 4).

Combining these results, a catalytic cycle can be proposed (Scheme 5) with **19** as the active species formed as the trans-isomer from both (*E*)- and (*Z*)-**6** and $Pd(PPh_3)_4$. Intermediate **19** reacts with the Grignard reagent under formation of **21** which, however, has never been directly detected in the reaction mixture. The formation of **21** may be facilitated by the polarization of the carbon–bromine bond in **19** as indicated (vide supra). Intermediate **21** then rapidly decomposes to (*E*)-**7** and $Pd(PPh_3)_2$ which is transferred to another molecule of **6**, thus completing the catalytic cycle. It should be pointed out that the transformation of **21**/**6** to **7**/**19** essentially corresponds to the substitution of an olefin in a palladium complex (**7** in **21**) by another olefin (**6**) which has ample precedent [17].

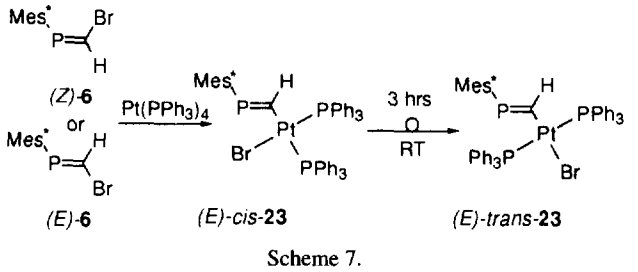
If no (*E*/*Z*)-**6** is present in the reaction mixture, **20** is formed by the reaction of **19** with phenylmagnesium bromide. Product **20** has never been detected in the crude reaction mixture after completion of the Stille-type coupling leading to (*E*)-**7**; hence its formation must proceed much more slowly than the formation of (*E*)-**7**.

A possible mechanism for the formation of **20** from **21** is depicted in Scheme 6. Compound **21** is proposed to rearrange to **22**, which is the product of a shift of a phenyl substituent from one triphenylphosphine ligand to the palladium center under simultaneous P–P bond formation. A similar mechanism has recently been suggested by Norton and coworkers in the case of phenyl- and methylpalladium iodides [18]. Reductive elimination of palladium leads to the final product **20**.

It is important to point out that for the completion of the coupling reactions furnishing compounds **7**–**17** or **20**, two equivalents of Grignard reagent are needed. The addition of only one equivalent of Grignard reagent furnishes a mixture of the coupling product and starting material in a 1 : 1 ratio. The proposed mechanism for the formation of the coupling product does not show the necessity for the use of two equivalents of Grignard reagent; the reason for this is not fully understood at the moment.

Intrigued by these results, and in search of further evidence for our proposed mechanism for the formation of **7**–**17** and **20**, we performed the analogous reaction of **6** with $Pt(PPh_3)_4$ in the hope of generating stable intermediates; the presence of satellites due to the coupling of the present $^{31}$P nuclei with the $^{195}$Pt center was expected to give additional information. However, the addition of $Pt(PPh_3)_4$ to (*Z*)-bromophosphaalkene (*Z*)-**6** in a 1 : 1 ratio in THF solution at room temperature led only to the formation of (*E*)-*trans*-**23** as a stable pink-colored solid (Scheme 7).

The $^{31}$P NMR spectrum unambiguously proved **23** to be the (*E*)-trans-complex with two identical triph-

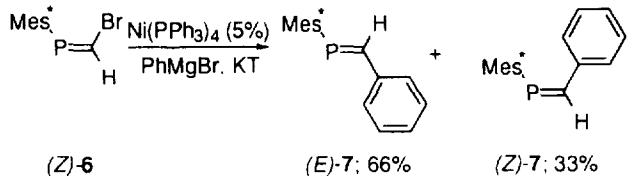



Scheme 7.

enylphosphine ligands; it shows a signal at $\delta(^{31}P, CDCl_3) = 273$ (t, $^2J(PH) = 26$ Hz, $^3J(PP) = 39$ Hz, $^2J(PPt) = 424$ Hz) and one at $\delta(^{31}P) = 27$ (d, $^3J(PP) = 39$ Hz, $^1J(PPt) = 3083$ Hz). However, when the crude reaction mixture was measured directly after mixing the two reagents, broad signals attributable to an intermediate product were found at $\delta(^{31}P) = 261$ with $^2J(PPt) = 247$ Hz, and this intermediate rearranged to the final product **23** within 3 h at room temperature. The intermediate probably is the cis-complex (*E*)-*cis*-**23**. This type of intermediate was also found in the formation of a platinum complex from Mes*P=$CCl_2$ [12d]. Additional proof for the (*E*)-configuration of intermediate (*E*)-*cis*-**23** was obtained from the analogous reaction of $Pt(PPh_3)_4$ with (*E*)-**6**; both (*E*)-*cis*-**23** and (*E*)-*trans*-**23** were observed, exactly as in the case of the reaction with (*Z*)-**6**. Apparently, a rapid isomerization of the (*Z*)- to the (*E*)-platinum compounds occurs, showing again the high susceptibility of the P=CBr unit to undergo isomerization in this type of reaction. Thus it turned out that, unexpectedly, platinum(0) forms the expected oxidative addition product of **6** where palladium(0) forms an $\eta^2$-complex. It is conceivable that the formation of the insertion product **23** with platinum proceeds via an $\eta^2$-complex comparable with **19**. Such a sequence has indeed been proposed by Mathey and coworkers [11b] for the oxidative addition of Pd(0) to 2-bromophosphinines.

In cases where palladium(0) catalysts can be applied, nickel(0) catalysts are usually active too. The catalyst $Ni(PPh_3)_4$ (5%) was generated in situ by the addition of four equivalents of triphenylphosphine to a solution of $Ni(cod)_2$ in THF. After addition of (*Z*)-**6** and two equivalents of phenylmagnesium bromide, the reaction was stirred overnight. Surprisingly, this coupling reaction produced two isomers of **7** in an *E*:*Z* ratio of 2:1 (Scheme 8), which was isolated as white crystals in 88% yield. Thus, for all three metals of Group 10, a different course of reaction was observed, and it may well be that three different mechanisms apply.

It is evident that the mechanism of this synthetically useful reaction is not yet fully understood. It appears to be different from the normal Stille-type coupling reactions and seems to be more complex; detailed investigations are clearly required.




(*Z*)-**6** (*E*)-**7**; 66% (*Z*)-**7**; 33%

Scheme 8.

## 3. Conclusion

A convenient method for the synthesis of various aryl-, alkenyl-, and alkynyl-substituted phosphaalkenes of the type (*E*)-Mes*P=C(H)R (**7–17**) has been developed using a Stille-type palladium(0) catalyzed coupling reaction of bromophosphaalkenes Mes*P=C(H)Br ((*E*/*Z*)-**6**) with Grignard reagents (RMgBr). Since we were primarily interested in (*E*)-products, we initially developed a new synthesis of (*E*)-bromophosphaalkene (*E*)-**6**. During these investigations, we found that, unexpectedly, the pure (*E*)-coupling products were also obtained when (*Z*)-bromophosphaalkene (*Z*)-**6** was coupled with Grignard reagents. To our knowledge, this type of inversion in a Stille coupling reaction is without precedent. In certain cases, where the Grignard reagent contains an ortho substituent (entry 4, Table 1), (*E*)-**6** gave better results. However, the synthesis of this isomer is more time consuming, which makes the use of (*Z*)-**6** more attractive for preparative purposes.

We have attempted to clarify the mechanism of the coupling reaction. Bromophosphaalkenes appeared to show an unusual reactivity with complexes of the type $Pd(PPh_3)_4$ and $Ni(PPh_3)_4$, which is different from the conventional Stille-type coupling reactions, and apparently proceeds via $\eta^2$-complexes of the phosphaalkene and not via the usual oxidative addition step. Further mechanistic investigations are in progress.

## 4. Experimental

### 4.1. General

All experiments were performed in oven-dried glassware ($T = 150°C$) and under a nitrogen atmosphere. NMR spectra were recorded on a Bruker WM 250 spectrometer ($^{31}P$: 101.25 MHz) and a Bruker AC 200 spectrometer ($^{13}C$: 50.32 MHz, $^1H$: 200.13 MHz). High resolution mass spectra were recorded on a Finnigan MAT5 spectrometer. All solvents were dried by distillation prior to use (diethyl ether and pentane from $LiAlH_4$, THF from $LiAlH_4$ and from sodium–benzophenone). Elemental analyses were performed by Microanalytisches Labor Pascher, Remagen-Bandorf, Germany. All new compounds were subjected to elemental analysis and HRMS, except for (*E*)-**12** and (*E*)-**16** owing to impurities. In these cases the exact mass was determined only. Compounds **1** [8b], (*Z*)-**3** [2e,8b], (*Z*)-**6** [2c] were prepared according to literature procedures.

### 4.2. Synthesis of (E)-bromomethylene-(2,4,6-tri-tert-butylphenyl)-phosphane ((E)-6)

A solution of *n*-butyllithium in hexane (11.1 ml; 1.6 M; 17.8 mmol) was added dropwise to a solution of

(*Z*)-**3** (6.6 g; 17.8 mmol) in THF (150 ml) at −110°C. The reaction mixture was stirred for 15 min at the same temperature. After the addition of 1,2-dibromoethane (3.34 g; 1.53 ml), the reaction mixture was slowly warmed to room temperature. At room temperature, a solution of lithiummethoxide in methanol (20 ml; 1 M; 20 mmol) was added and the reaction mixture was stirred at ambient temperature for an additional hour. 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 (*Z*)-**3** as colorless crystals (yield: 3.9 g; 10.7 mmol; 60%) with the by-product **5** (40%) in the motherliquor; m.p. 73–77°C. $^1$H NMR ($CDCl_3$): δ 1.33 (s, 9H, *para*-$^t$Bu), 1.50 (s, 18H, *ortho*-$^t$Bu), 7.41 (d, 1H, $^2J$(HP) = 24.1 Hz, P=C*H*), 7.41 (d, 2H, $^4J$(HP) = 1.3 Hz, Ar*H*). $^{13}$C{$^1$H} NMR ($CDCl_3$): δ 31.2 (s, *para*-C(*C*H$_3$)$_3$), 33.7 (d, $^4J$(CP) = 7.2 Hz, *ortho*-C(*C*H$_3$)$_3$), 34.9 (s, *para*-*C*(CH$_3$)$_3$), 38.0 (s, *ortho*-*C*(CH$_3$)$_3$), 121.8 (d, $^3J$(CP) = 1.0 Hz, *meta*-Ar*C*), 137.1 (d, $^1J$(CP) = 56.8 Hz, *ipso*-Ar*C*), 147.6 (d, $^1J$(CP) = 49.8 Hz, P=C), 150.4 (s, *para*-Ar*C*), 153.9 (d, $^2J$(CP) = 2.2 Hz, *ortho*-Ar*C*). $^{31}$P NMR ($CDCl_3$): δ 262. Spectra were identical with those reported [2b–e].

### 4.3. General procedure for the synthesis of 7–17

A solution of the Grignard reagent in THF (10 ml; 4 M; 4 mmol) was prepared by reacting the organic bromide (4 mmol) with magnesium metal (5 mmol) in THF (10 ml). In the case of **15** and **17**, the Grignard reagent was prepared in a different way; furane or phenyacetylene was first lithiated and subsequently transmetallated by the addition of a solution of magnesium bromide. The Grignard reagent was added to a solution of (*Z*)-**6** (0.74 g; 2 mmol) and $Pd_2(dba)_3$–$PPh_3$ (5 mol% Pd) in THF (5 ml). The reaction mixture was stirred as indicated in Table 1 and the progression of the reaction was monitored by $^{31}$P NMR spectroscopy of the crude reaction mixture. After completion of the reaction, the solvent was evaporated and the residue dissolved in dichloromethane. The reaction mixture was adsorbed on silical gel by adding silica gel and evaporation of the dichloromethane. The mixture was added on top of a short column of silica. After flushing the column with pentane or diethyl ether the eluent was evaporated and the product crystallized from pentane.

#### 4.3.1. (E)-Phenylmethylene-(2,4,6-tri-tert-butylphenyl)-phosphane ((E)-7)

Colorless crystals (yield: 0.66 g; 1.8 mmol; 90%); m.p. 153–154°C. $^1$H NMR ($CDCl_3$): δ 1.32 (s, 9H, *para*-$^t$Bu), 1.46 (s, 18H, *ortho*-$^t$Bu), 7.41 (d, 2H, $^4J$(HP) = 1.2 Hz, Ar*H*), 7.22–7.50 (m, 5H, Ph*H*), 8.09 (d, 1H, $^2J$(HP) = 25.6 Hz, P=C*H*). $^{31}$P NMR ($CDCl_3$): δ 259. MS (70 eV): *m/z* (%) = 366 (12) ($M^+$), 309 (6) ($M^+ - {}^t$Bu), 351 (4) ($M^+$ − Me). HRMS: calc. for $C_{25}H_{35}P$ 366.2477, found 366.2473. Spectra were identical with those reported [2e,13].

#### 4.3.2. (E)-4-(Methyl)phenylmethylene-(2,4,6-tri-tert-butylphenyl)-phosphane ((E)-8)

Colorless crystals (yield: 0.68 g; 1.8 mmol; 90%); m.p. 146–148°C. $^1$H NMR ($CDCl_3$): δ 1.39 (s, 9H, *para*-$^t$Bu), 1.55 (s, 18H, *ortho*-$^t$Bu), 2.35 (d, 3H, $^7J$(HP) = 2.46 Hz, Me), 7.14 (d, 2H, $^3J(H_{a,b})$ = 7.9 Hz, *meta*-Ph*H*), 7.47 (d, 2H, $^4J$(HP) = 1.1 Hz, Ar*H*), 7.50 (dd, 2H, $^3J(H_{a,b})$ = 7.9 Hz, $^4J$(HP) = 3.6 Hz, *ortho*-Ph*H*), 8.14 (d, 1H, $^2J$(HP) = 25.6 Hz, P=C*H*). $^{13}$C{$^1$H} NMR ($CDCl_3$): δ 21.2 (s, Me), 31.2 (s, *para*-C(*C*H$_3$)$_3$), 33.7 (d, $^4J$(CP) = 7.1 Hz, *ortho*-C(*C*H$_3$)$_3$), 34.9 (s, *para*-*C*(CH$_3$)$_3$), 38.2 (s, *ortho*-*C*(CH$_3$)$_3$), 121.7 (s, *meta*-Ar*C*), 125.6 (d, $^3J$(CP) = 21.8 Hz, *ortho*-Ph*C*), 129.3 (d, $^4J$(CP) = 2.3 Hz, *meta*-Ph*C*), 137.4 (d, $^2J$(CP) = 13.6 Hz, *ipso*-Ph*C*), 137.9 (d, $^5J$(CP) = 7.7 Hz, *para*-Ph*C*), 138.9 (d, $^1J$(CP) = 53.6 Hz, *ipso*-Ar*C*), 149.4 (s, *para*-Ar*C*), 153.9 (s, *ortho*-Ar*C*), 175.8 (d, $^1J$(CP) = 34.2 Hz, P=*C*). $^{31}$P NMR ($CDCl_3$): δ 254. MS (70 eV): *m/z* (%) = 380 (13) ($M^+$). HRMS: calc. for $C_{26}H_{37}P$ 380.2633, found 380.2631. Anal. Found: C, 81.98; H, 9.83; P, 8.05. $C_{26}H_{37}P$. Calc.: C, 82.06; H, 9.81; P, 8.14%.

#### 4.3.3. (E)-2-(Methoxy)phenylmethylene-(2,4,6-tri-tert-butylphenyl)-phosphane ((E)-9)

Colorless crystals (yield: 0.70 g; 1.76 mmol; 88%); m.p. 113–114°C. $^1$H NMR ($CDCl_3$): δ 1.33 (s, 9H, *para*-$^t$Bu), 1.50 (s, 18H, *ortho*-$^t$Bu), 3.79 (s, 3H, MeO), 6.8–6.9 (m, 2H, Ph*H*), 7.1–7.2 (m, 1H, Ph*H*), 7.41 (s, 2H, Ar*H*), 7.7 (m, 1H, Ph*H*), 8.33 (d, 1H, $^2J$(HP) = 25.7 Hz, P=C*H*). $^{13}$C{$^1$H} NMR ($CDCl_3$): δ 31.4 (s, *para*-C(*C*H$_3$)$_3$), 33.8 (d, $^4J$(CP) = 7.6 Hz, *ortho*-C(*C*H$_3$)$_3$), 34.9 (s, *para*-*C*(CH$_3$)$_3$), 38.2 (d, $^3J$(CP) = 8.8 Hz, *ortho*-*C*(CH$_3$)$_3$), 55.3 (s, MeO), 110.9 (d, $^4J$(CP) = 2.9 Hz, *meta*-Ph*C*), 120.6 (d, $^5J$(CP) = 2.9 Hz, *para*-Ph*C*), 121.6 (s, *meta*-Ar*C*), 126.7 (d, $^3J$(CP) = 24.5 Hz, *ortho*-Ph*C*), 128.8 (d, $^4J$(CP) = 7.1 Hz, *meta*-Ph*C*), 129.6 (d, $^2J$(CP) = 11.9 Hz, *ipso*-Ph*C*), 140.7 (d, $^1J$(CP) = 55.2 Hz, *ipso*-Ar*C*), 149.2 (s, *para*-Ar*C*), 153.8 (d, $^2J$(CP) = 1.6 Hz, *ortho*-Ar*C*), 155.5 (d, $^3J$(CP) = 11.9 Hz, *ortho*-Ph*C*), 170.5 (d, $^1J$(CP) = 37.0 Hz, P=*C*). $^{31}$P NMR ($CDCl_3$): δ 261. MS (70 eV): *m/z* (%) = 396 (21) ($M^+$), 381 (6) ($M^+$ − Me), 365 (1) ($M^+$ − MeO). HRMS: calc. for $C_{26}H_{37}OP$ 396.2582, found 396.2583. Anal. Found: C, 78.50; H, 9.41; P, 7.78. $C_{26}H_{37}OP$. Calc.: C, 78.74; H, 9.41; P, 7.81%. Spectra were identical with those reported [13a].

#### 4.3.4. (E)-2-N,N-(dimethylamino)phenylmethylene-(2,4,6-tri-tert-butylphenyl)-phosphane ((E)-10)

Yellow crystals (yield: 0.45 g; 1.1 mmol; 55%); m.p. 130–132°C. $^1$H NMR ($CDCl_3$): δ 1.29 (s, 9H, *para*-

$^t$Bu), 1.46 (s, 18H, *ortho*-$^t$Bu), 2.53 (s, 6H, Me), 6.9–7.0 (m, 2H, PhH), 7.0–7.1 (m, 1H, PhH), 7.35 (s, 2H, ArH), 7.8–7.9 (m, 1H, PhH), 8.33 (d, 1H, $^2J$(HP) = 25.2 Hz, P=CH). $^{13}$C{$^1$H} NMR ($CDCl_3$): δ 31.2 (s, *para*-C($CH_3$)$_3$), 33.8 (d, $^4J$(CP) = 7.3 Hz, *ortho*-C($CH_3$)$_3$), 34.8 (s, *para*-$C$($CH_3$)$_3$), 38.2 (s, *ortho*-$C$($CH_3$)$_3$), 45.0 (s, Me), 118.7 (d, $J$(CP) = 2.2 Hz, PhC), 121.5 (s, *meta*-ArC), 122.7 (d, $J$(CP) = 2.2 Hz, PhC), 126.9 (d, $J$(CP) = 27.4 Hz, PhC), 128.5 (d, $J$(CP) = 6.4 Hz, PhC), 139.7 (d, $^1J$(CP) = 53.3 Hz, *ipso*-ArC), 149.2 (s, *para*-ArC), 150.7 (d, $J$(CP) = 13.2 Hz, PhC), 153.9 (s, $^2J$(CP) = 1.8 Hz, *ortho*-ArC), 172.3 (d, $^1J$(CP) = 35.1 Hz, P=C). $^{31}$P NMR ($CDCl_3$): δ = 255. MS (70 eV): *m/z* (%) = 409 (0.16) ($M^+$). HRMS: calc. for $C_{27}H_{40}NP$ 409.2898, found 409.2902. Anal. Found: C, 79.18; H, 10.09; P, 7.47. $C_{27}H_{40}NP$. Calc: C, 79.17; H, 9.85; P, 7.56%.

#### 4.3.5. (E)-4-N,N-(Dimethylamino)phenylmethylene-(2,4,6-tri-tert-butylphenyl)-phosphane ((E)-11)

Yellow crystals (yield: 0.74 g; 1.8 mmol; 90%); m.p. 204–206°C. $^1$H NMR ($CDCl_3$): δ 1.43 (s, 9H, *para*-$^t$Bu), 1.60 (s, 18H, *ortho*-$^t$Bu), 3.02 (s, 6H, Me), 6.71 (d, 2H, $^3J(H_{a,b})$ = 8.9 Hz, *meta*-PhH), 7.57 (d, 2H, $^4J$(HP) = 1.3 Hz, ArH), 7.50 (dd, 2H, $^3J(H_{a,b})$ = 8.9 Hz, $^4J$(HP) = 3.4 Hz, *ortho*-PhH), 8.12 (d, 1H, $^2J$(HP) = 25.3 Hz, P=CH). $^{13}$C{$^1$H} NMR ($CDCl_3$): δ 31.2 (s, *para*-C($CH_3$)$_3$), 33.7 (d, $^4J$(CP) = 7.1 Hz, *ortho*-C($CH_3$)$_3$), 34.9 (s, *para*-$C$($CH_3$)$_3$), 38.3 (s, *ortho*-$C$($CH_3$)$_3$), 40.3 (s, Me), 112.1 (d, $^4J$(CP) = 2.2 Hz, *meta*-PhC), 121.5 (s, *meta*-ArC), 127.0 (d, $^3J$(CP) = 21.7 Hz, *ortho*-PhC), 129.3 (d, $^2J$(CP) = 13.2 Hz, *ipso*-PhC), 139.9 (d, $^1J$(CP) = 53.4 Hz, *ipso*-ArC), 149.1 (s, *para*-ArC), 150.3 (d, $^5J$(CP) = 6.3 Hz, *para*-PhC), 154.0 (s, *ortho*-ArC), 176.3 (d, $^1J$(CP) = 33.9 Hz, P=C). $^{31}$P NMR ($CDCl_3$): δ = 233. MS (70 eV): *m/z* (%) = 409 (23) ($M^+$), 352 (2) ($M^+ - {}^t$Bu). HRMS: calc. for $C_{27}H_{40}NP$ 409.2898, found 409.2900. Anal. Found: C, 79.08; H, 9.79; P, 7.56. $C_{27}H_{40}NP$. Calc.: C, 79.17; H, 9.85; P, 7.56%. Spectra were identical with those reported [13a].

#### 4.3.6. (E)-3-N,N-(Diethylaminomethyl)phenylmethylene-(2,4,6-tri-tert-butylphenyl)-phosphane ((E)-12)

After isolation of the product, the product was dissolved in dichloromethane and washed with a saturated solution of $NaHCO_3$ in water furnishing a yellow oil after evaporation of the dichloromethane layer (yield: 0.81 g; 1.8 mmol; 90%). $^1$H NMR ($CDCl_3$): δ 1.12 (t, 6H, $^3J$(HH) = 7.1 Hz, $CH_2CH_3$), 1.45 (s, 9H, *para*-$^t$Bu), 1.62 (s, 18H, *ortho*-$^t$Bu), 2.61 (q, 4H, $^3J$(HH) = 7.1 Hz, $CH_2CH_3$), 3.64, (br.s, 2H, $CH_2$), 7.24–7.49 (m, 4H, PhH), 7.57 (d, 2H, $^4J$(HP) = 0.7 Hz, ArH), 8.22 (d, 1H, $^2J$(HP) = 25.5 Hz, P=CH). $^{13}$C{$^1$H} NMR ($CDCl_3$): δ 11.7 (s, $CH_2$), 31.4 (s, *para*-C($CH_3$)$_3$), 33.9 (d, $^4J$(CP) = 7.1 Hz, *ortho*-C($CH_3$)$_3$), 34.9 (s, *para*-$C$($CH_3$)$_3$), 38.2 (s, *ortho*-$C$($CH_3$)$_3$), 46.7 (s, $CH_2CH_3$), 57.4 (s, $CH_2CH_3$), 121.7 (s, *meta*-ArC), 124.0 (d, $J$(CP) = 22.4 Hz, PhC), 127.3 (d, $J$(CP) = 21.3 Hz, PhC), 132.0 (d, $J$(CP) = 9.9 Hz, PhC), 139.5 (d, $^1J$(CP) = 82.9 Hz, *ipso*-ArC), 149.5 (s, *para*-ArC), 154.0 (s, *ortho*-ArC), 176.3 (d, $^1J$(CP) = 34.7 Hz, P=C). $^{31}$P NMR ($CDCl_3$): δ = 258. MS (70 eV): *m/z* (%) = 451 (16) ($M^+$). HRMS: calc. for $C_{30}H_{46}NP$ 451.3369, found 451.3374. As the compound was impure, no elemental analysis is available.

#### 4.3.7. (E)-4-(Fluorophenyl)methylene-(2,4,6-tri-tert-butylphenyl)-phosphane ((E)-13)

Colorless crystals (yield: 0.69 g; 1.8 mmol; 90%); m.p. 125–127°C. $^1$H NMR ($CDCl_3$): δ 1.43 (s, 9H, *para*-$^t$Bu), 1.59 (s, 18H, *ortho*-$^t$Bu), 7.03 (dd, 2H, $^3J(H_{a,b})$ = 8.5 Hz, $^3J$(HF) = 8.5 Hz, *meta*-PhH), 7.53 (d, 2H, $^4J$(HP) = 1.1 Hz, ArH), 7.5–7.6 (m, 2H, $^3J(H_{a,b})$, $^4J$(HP), $^4J$(HF), *ortho*-PhH), 8.15 (d, 1H, $^2J$(HP) = 25.7 Hz, P=CH). $^{13}$C{$^1$H} NMR ($CDCl_3$): δ 31.3 (s, *para*-C($CH_3$)$_3$), 33.7 (d, $^4J$(CP) = 7.1 Hz, *ortho*-C($CH_3$)$_3$), 34.9 (s, *para*-$C$($CH_3$)$_3$), 38.2 (s, *ortho*-$C$($CH_3$)$_3$), 115.6 (dd, $^4J$(CP) = 2.9 Hz, $^2J$(CF) = 21.7 Hz, *meta*-PhC), 121.8 (s, *meta*-ArC), 127.2 (dd, $^3J$(CP) = 22.1 Hz, $^3J$(CF) = 7.7 Hz, *ortho*-PhC), 136.4 (dd, $^2J$(CP) = 14.1 Hz, $^4J$(CF) = 3.6 Hz, *ipso*-PhC), 138.6 (d, $^1J$(CP) = 53.1 Hz, *ipso*-ArC), 149.6 (s, *para*-ArC), 154.8 (d, $^2J$(CP) = 1.4 Hz, *ortho*-ArC), 162.5 (dd, $^5J$(CP) = 8.4 Hz, $^1J$(CF) = 248.3 Hz, *para*-PhC), 174.4 (d, $^1J$(CP) = 32.6 Hz, P=C). $^{31}$P NMR ($CDCl_3$): δ 257. MS (70 eV): *m/z* (%) = 384 (8.9) ($M^+$), 369 (2) ($M^+$ – Me). HRMS: calc. for $C_{25}H_{34}PF$ 384.2382, found 384.2379. Anal. Found: C, 78.13; H, 9.07; P, 7.95. $C_{25}H_{34}FP$. Calc.: C, 78.09; H, 8.92; P, 8.05%. Spectra were identical with those reported [13a].

#### 4.3.8. (E)-Thienylmethylene-(2,4,6-tri-tert-butylphenyl)-phosphane ((E)-14)

Yellowish crystals (yield: 0.66 g; 1.78 mmol; 89%); m.p. 104–105°C. $^1$H NMR ($CDCl_3$): δ 1.48 (s, 9H, *para*-$^t$Bu), 1.65 (s, 18H, *ortho*-$^t$Bu), 7.0–7.1 (m, 2H), 7.2–7.3 (m, 1H), 7.57 (s, 2H, ArH), 8.25 (d, 1H, $^2J$(HP) = 24.1 Hz, P=CH). $^{13}$C{$^1$H} NMR ($CDCl_3$): δ 31.5 (s, *para*-C($CH_3$)$_3$), 34.0 (d, $^4J$(CP) = 6.8 Hz, *ortho*-C($CH_3$)$_3$), 35.1 (s, *para*-$C$($CH_3$)$_3$), 38.4 (s, *ortho*-$C$($CH_3$)$_3$), 121.8 (d, $^3J$(CP) = 1.2 Hz, *meta*-ArC), 124.9 (d, $J$(CP) = 14.3 Hz, ThienylC), 125.6 (d, $J$(CP) = 22.7 Hz, ThienylC), 127.8 (d, $J$(CP) = 4.2 Hz, ThienylC), 138.5 (d, $^1J$(CP) = 53.2 Hz, *ipso*-ArC), 145.2 (d, $^2J$(CP) = 14.7 Hz, ThienylC), 149.9 (s, *para*-ArC), 154.3 (s, *ortho*-ArC), 166.3 (d, $^1J$(CP) = 30.6 Hz, P=C). $^{31}$P NMR ($CDCl_3$): δ 247. MS (70 eV): *m/z* (%) = 372 (12) ($M^+$). HRMS: calc. for $C_{23}H_{33}P^{32}S$ 372.2041, found 372.2040. Anal. Found: C, 73.96; H, 8.88; P, 8.06. $C_{23}H_{33}PS$. Calc.: C, 74.15; H, 8.93; P, 8.31%.

*4.3.9. (E)-Furylmethylene-(2,4,6-tri-tert-butylphenyl)-phosphane ((E)-15)*

A solution of *n*-butyllithium in hexane (2.5 ml; 1.6 M; 4 mmol) was added to a solution of furan (0.27 g; 4 mmol) in THF (4 ml) at 0°C. The reaction mixture was warmed to room temperature and stirred for a further 15 min. A solution of magnesium bromide in THF (10 ml; 0.4 ml; 4 mmol), was added furnishing the Grignard reagent. The Grignard reagent was used as described above. Colorless crystals (yield: 0.62 g; 1.74 mmol; 87%); m.p. 142–143°C. $^1$H NMR ($CDCl_3$): δ 1.49 (s, 9H, *para*-$^t$Bu), 1.67 (s, 18H, *ortho*-$^t$Bu), 6.30 (m, 1H, furyl*H*), 6.48 (m, 1H, furyl*H*), 7.49 (m, 1H, furyl*H*), 7.58 (d, 2H, $^2J$(HP) = 1.0 Hz, Ar*H*), 7.87 (d, 1H, $^2J$(HP) = 24.1 Hz, P=C*H*). $^{13}$C{$^1$H} NMR ($CDCl_3$): δ 31.4 (s, *para*-C($CH_3$)$_3$), 33.9 (d, $^4J$(CP) = 7.2 Hz, *ortho*-C($CH_3$)$_3$), 35.0 (s, *para*-*C*($CH_3$)$_3$), 38.3 (s, *ortho*-*C*($CH_3$)$_3$), 108.9 (d, *J*(CP) = 22.1 Hz, furyl*C*), 112.0 (d, *J*(CP) = 4.0 Hz, furyl*C*), 121.7 (s, *meta*-Ar*C*), 139.1 (d, $^1J$(CP) = 53.1 Hz, *ipso*-Ar*C*), 142.7 (d, *J*(CP) = 10.7 Hz, furyl*C*), 149.6 (s, *para*-Ar*C*), 154.2 (s, *ortho*-Ar*C*), 155.9 (d, $^2J$(CP) = 8.9 Hz, furyl*C*), 159.1 (d, $^1J$(CP) = 34.2 Hz, P=*C*). $^{31}$P NMR ($CDCl_3$): δ 243. MS (70 eV): *m/z* (%) = 356 (15) ($M^+$). HRMS: calc. for $C_{23}H_{33}OP$ 356.2269, found 356.2270. Anal. Found: C, 77.68; H, 9.28; P, 8.62. $C_{23}H_{33}OP$. Calc.: C, 77.49; H, 9.34; P, 8.69%.

*4.3.10. (E)-1-(2,4,6-Tri-tert-butylphenyl)-1-phosphabutadiene ((E)-16)*

Green oil (yield: 0.27 g; 0.86 mmol; 43%) $^1$H NMR ($CDCl_3$): δ 1.44 (s, 9H, *para*-$^t$Bu), 1.59 (s, 18H, *ortho*-$^t$Bu), 5.14 (d, 1H, $^2J$(HH) = 6.7 Hz, Olefinic*H*), 5.22 (d, 1H, $^2J$(HH) = 6.2 Hz, Olefinic*H*), 6.8–7.1 (m, 1H, Olefinic*H*), 7.51 (s, 2H, Ar*H*), 7.90 (dd, 1H, $^2J$(HP) = 24.7 Hz, $^3J$(HH) = 12.9 Hz, P=C*H*). $^{13}$C{$^1$H} NMR ($CDCl_3$): δ 31.6 (s, *para*-C($CH_3$)$_3$), 33.9 (d, $^4J$(CP) = 7.0 Hz, *ortho*-C($CH_3$)$_3$), 35.1 (s, *para*-*C*($CH_3$)$_3$), 38.3 (s, *ortho*-*C*($CH_3$)$_3$), 117.1 (d, $^3J$(CP) = 39.0 Hz, Olefinic*C*), 121.7 (s, *meta*-Ar*C*), 138.2 (d, $^3J$(CP) = 26.3 Hz, Olefinic*C*), 139.1 (d, $^1J$(CP) = 53.4 Hz, *ipso*-Ar*C*), 149.7 (s, *para*-Ar*C*), 153.9 (s, *ortho*-Ar*C*), 176.2 (d, $^1J$(CP) = 31.1 Hz, P=*C*). $^{31}$P NMR ($CDCl_3$): δ 271. MS (70 eV): *m/z* (%) = 316 (88) ($M^+$), 289 (1) ($M^+ - C_2H_3$). HRMS: calc. for $C_{21}H_{33}P$ 316.2320, found 316.2322. Owing to impurities and the instability of the product, no elemental analysis could be obtained.

*4.3.11. (E)-(Phenylethynyl)methylene-(2,4,6-tri-tert-butylphenyl)-phosphane ((E)-17)*

A solution of *n*-butyllithium in hexane (2.5 ml; 1.6 M; 4 mmol) was added to a solution of phenylacetylene (0.41 g; 4 mmol) in THF (4 ml) at 0°C. The reaction mixture was warmed to room temperature and was stirred for a further 15 min. A solution of magnesium bromide in THF (10 ml; 0.4 ml; 4 mmol) was added furnishing the Grignard reagent. The Grignard reagent was used as described above. Colorless crystals (yield: 0.69 g; 1.76 mmol; 88%); m.p. 135–137°C. $^1$H NMR ($CDCl_3$): δ 1.32 (s, 9H, *para*-$^t$Bu), 1.56 (s, 18H, *ortho*-$^t$Bu), 6.92 (m, 3H, Ph*H*), 7.40 (m, 2H, Ph*H*), 7.41 (d, 1H, $^2J$(HP) = 23.0 Hz, P=C*H*), 7.57 (d, 2H, $^4J$(HP) = 0.9 Hz, Ar*H*). $^{13}$C{$^1$H} NMR ($CDCl_3$): δ 31.3 (s, *para*-C($CH_3$)$_3$), 33.9 (d, $^4J$(CP) = 7.0 Hz, *ortho*-C($CH_3$)$_3$), 34.9 (s, *para*-*C*($CH_3$)$_3$), 38.1 (s, *ortho*-*C*($CH_3$)$_3$), 90.7 (d, $^3J$(CP) = 18.9 Hz, ethynyl*C*), 102.5 (d, $^2J$(CP) = 15.7 Hz, ethynyl*C*), 121.7 (s, *meta*-Ar*C*), 123.8 (d, $^4J$(CP) = 7.40 Hz, *ipso*-Ph*C*), 128.1 (d, *J*(CP) = 2.31 Hz, Ph*C*), 128.2 (s, Ph*C*), 131.2 (d, *J*(CP) = 6.03 Hz, Ph*C*), 138.4 (d, $^1J$(CP) = 60.0 Hz, *ipso*-Ar*C*), 150.1 (s, *para*-Ar*C*), 151.5 (d, $^1J$(CP) = 30.3 Hz, P=*C*), 153.9 (s, *ortho*-Ar*C*). $^{31}$P NMR ($CDCl_3$): δ 315. MS (70 eV): *m/z* (%) = 390 (5) ($M^+$), 375 (6) ($M^+ - Me$), 333 (6) ($M^+ - {}^t$Bu). HRMS: calc. for $C_{27}H_{35}P$ 390.2477, found 390.2477. Anal. Found: C, 83.03; H, 9.13; P, 7.95. $C_{27}H_{35}P$. Calc.: C, 83.03; H, 9.04; P, 7.93%.

*4.4. Synthesis of complex $\eta^2$-(Mes*P=CHBr)Pd($PPh_3$)$_2$ (19)*

A solution of (*Z*)-**6** (0.45 g; 1.2 mmol) in THF (4.0 ml) was added to a suspension of $Pd(PPh_3)_4$ (1.40 g; 1.21 mmol) in THF (6.0 ml) at room temperature. After 15 min of stirring the solvent was evaporated and the solid residue washed with pentane. Drying the residue in vacuo furnished a yellow powder which was contaminated with minor amounts of triphenylphosphine oxide. Yellow powder (yield: 0.8 g; 0.8 mmol; 67%). $^1$H NMR ($CDCl_3$) δ 2.7 (dd, *J*(HP) = 8.5 Hz; *J*(HP) = 2.1 Hz). $^{31}$P{$^1$H} NMR ($CDCl_3$) = 64.8 (dd, *J*(PP) = 104.8 Hz, *J*(PP) = 8.1 Hz), 24.5 (dd, *J*(PP) = 8.1 Hz, *J*(PP) = 6.7 Hz), and 21.9 (dd, *J*(PP) = 104.8 Hz, *J*(PP) = 6.7 Hz).

*4.5. Synthesis of (E)-Mes*P=C(H)PtBr($PPh_3$)$_2$ ((E)-trans-23)*

A solution of (*Z*)-**6** (0.69 g; 1.86 mmol) in THF (2.0 ml) was added to a suspension of $Pt(PPh_3)_4$ (2.31 g; 1.86 mmol) in THF (6.0 ml) at room temperature. After 3 h of stirring at ambient temperature the solvent was evaporated and the solid residue was washed with pentane. Drying the residue in vacuo furnished a pink-colored powder (yield: 1.52 g; 1.40 mmol; 75%); m.p. 183–185°C. $^1$H NMR ($CDCl_3$) δ 1.09 (s, 18 H, *ortho*-$^t$Bu), 1.33 (s, 9 H, *para*-$^t$Bu), 7.24–7.36 (m, 30 H, $PPh_3$), 8.51 (d, 1H, $^2J$(HP) = 26 Hz, P=C*H*). $^{13}$C{$^1$H} NMR ($CDCl_3$): δ 31.5 (s, *para*-C($CH_3$)$_3$), 33.3 (s, *ortho*-C($CH_3$)$_3$), 34.7 (s, *para*-*C*($CH_3$)$_3$), 37.6 (s, *ortho*-*C*($CH_3$)$_3$), 120.6 (s, *meta*-Ar*C*), 127.6–135.4 (m, $PPh_3$), 148.1 (s, *para*-Ar*C*), 151.6 (s, *ortho*-Ar*C*),

182.9 (d, $^1J$(CP) = 78 Hz, P=*C*). $^{31}$P NMR ($CDCl_3$) = δ 273 (t, $^2J$(PH) = 26 Hz, $^3J$(PP) = 39 Hz, $^2J$(PPt) = 424 Hz), 27 (d, $^3J$(PP) = 39 Hz, $^1J$(PPt) = 3083 Hz). Anal. Found: C, 60.03; H, 5.67; P, 8.28; Pt, 17.1. $C_{55}H_{60}BrP_3Pt$. Calc.: C, 60.66; H, 5.56; P, 8.53; Pt, 17.9%.

### 4.6. Synthesis of a mixture of (Z)-7 and (E)-7

THF (2 ml) was added to a mixture of (*Z*)-**6** (0.37 g; 1.0 mmol), $Ni(cod)_2$ (0.015 g; 0.050 mmol) and triphenylphosphine (0.541 g; 0.405 mmol). To the deep-red–purple solution, a solution of phenyl magnesium bromide (2 mmol) in THF was added. The reaction was stirred at ambient temperature for one night. The reaction was worked up as described above. A mixture of (*Z*)-**7** and (*E*)-**7** was obtained in a ratio of 1 : 2 as white crystals after crystallization from pentane (yield: 0.32 g; 0.88 mmol; 88%).

### 4.7. Crystal structure determination of (E)-Furylmethylene-(2,4,6-tri-tert-butylphenyl)-phosphane ((E)-15)

Crystals of (*E*)-**15** were obtained by crystallization from pentane (mixed isomers). X-ray data were collected on a cut to size specimen (transparent, colorless, $0.20 \times 0.45 \times 0.51$ mm$^3$). Crystals were found to be intergrown/twinned. The selected specimen was considered to be, though poor, of sufficient quality for the purpose of this study. Data collection was done on a CAD4 T on rotating anode at 150 K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Unit cell parameters were derived from the setting angles of 19 reflections in the range $10 < \theta < 14°$. Crystals are monoclinic, space group $P2_1/c$, with four molecules in the unit cell ($a$ = 9.5197(7), $b$ = 9.6183(8), $c$ = 24.830(9) Å, β = 112.14(3)°, $V$ = 2105.9(8) Å$^3$, $d_x$ = 1.1249 g cm$^{-3}$, $F_{000}$ = 776). Intensity data (ω-scan, $\Delta\omega = 0.80 + 0.35 \tan\theta°$) were collected (6502) and averaged into a set of 4083 unique reflections of which 2560 with $I > 2\sigma(I)$. The structure was solved by direct methods (S1R [19a]) and refined of $F^2$ (positions and anisotropic thermal parameters of the non-hydrogen atoms with SHELXL-93 [19b]). Hydrogen atoms were taken into account at calculated positions. Convergence was reached at $R = 0.22$ for 235 parameters. There was no residual density outside $-0.67 < \Delta\rho < 1.00$ e Å$^{-3}$. Final coordinates are given in Table 2. Full details may be obtained from one of the authors (A.L.S). Fig. 1 gives a PLATON [19c] presentation of the molecule.

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