Synthesis of Novel Phosphaalkene-Based Bidentate Ligands Mes*P=CH(3-R-Ar) (R = Pyridyl, Carbaldimino) and Formation of Three-Membered Palladacycles Mes*(Me)P−CH(3-R-Ar)−PdCl by Carbapalladation of the P=C Double Bond†

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Novel functionalized phosphaalkene-based bidentate ligands of the type 1-[(*E*)-Mes*P=C(H)]-3-R-benzene (**8**, R = *N*-phenylcarbaldimino; **2**, R = 2-pyridyl; Mes* = 2,4,6-tri-*tert*-butylphenyl) were prepared via a Pd(0)-catalyzed cross-coupling reaction of (*Z*)-bromophosphaalkene (*Z*)-**1** with Grignard reagents. The reaction of **8** and **2** with MePdCl(COD) furnished three-membered phosphapalladacycles of the type Mes*(Me)P−CH(3-R-Ar)−PdCl (**9**, R = *N*-phenylcarbaldimino; **10**, R = 2-pyridyl), displaying intramolecular coordination between the phosphine ligand and palladium(II). The structure of **10** was established by an X-ray structure determination, showing a dimeric structure. The addition of triphenylphosphine to **9** and **10** causes rupture of the interconnecting Pd−N bonds, furnishing **11** and **12**, respectively.

Introduction

The development of the synthetic methodology for the preparation of phosphaalkenes and phosphinines has evolved into an important new area of organic chemistry that is presently finding its application in organometallic chemistry.[1−6] Phosphaalkenes and phosphinines, being the phosphorus analogues of the well-known imines and pyridines,[7−9] attract interest because of their unique coordinative properties.

A special class of phosphaalkenes which are kinetically stabilized by a bulky 2,4,6-tri-*tert*-butyl group (=supermesityl = Mes*) at the phosphorus atom of the P=C double bond has been applied in novel coordination chemistry: Yoshifuji et al. reported (1,2-diphosphinidenecyclobutene)palladium dichloride complexes and their application as homogeneous catalysts in a Heck reaction.[2c] Geoffroy et al.[1] developed the 1,3-bis(phosphaalkenyl)benzene ligand and Yoshifuji et al.[2d] the 1,3,4,6-tetrakis(phosphaalkenyl)benzene ligand, both of which underwent bicyclometalation with $PdCl_2(PhCN)_2$.

For some time, our group has been engaged in the development and application of halogen-substituted phosphaalkenes.[5] These reagents are expected to be useful synthons for the preparation of novel functionalized phosphaalkenes. Thus, their conversion into phosphavinylidene carbenoids and (phosphaalkenyl)-metal reagents has proved to be a versatile tool for further functionalization, but the functionalization was limited to C−C bond formation toward sp^3-hybridized carbon centers.[5a,b] For the preparation of bidentate

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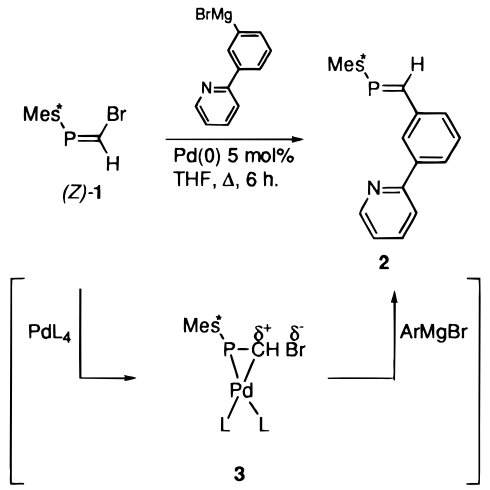
Scheme 1



ligand systems analogous to those mentioned above,[1,2c,d] the arylation of the phosphaalkene moiety would be required.

Recently we discovered a convenient method for the preparation of aryl-functionalized phosphaalkenes. The monobromophosphaalkene (*Z*)-Mes*P═CHBr ((*Z*)-**1**) was cross-coupled with aryl Grignard reagents in a Pd(0)-catalyzed reaction.[5c] The reverse mode of coupling was utilized in the preparation of pyridyl-functionalized phosphaalkenes, which were applied as bidentate ligands in novel Pd(II) complexes.[5d]

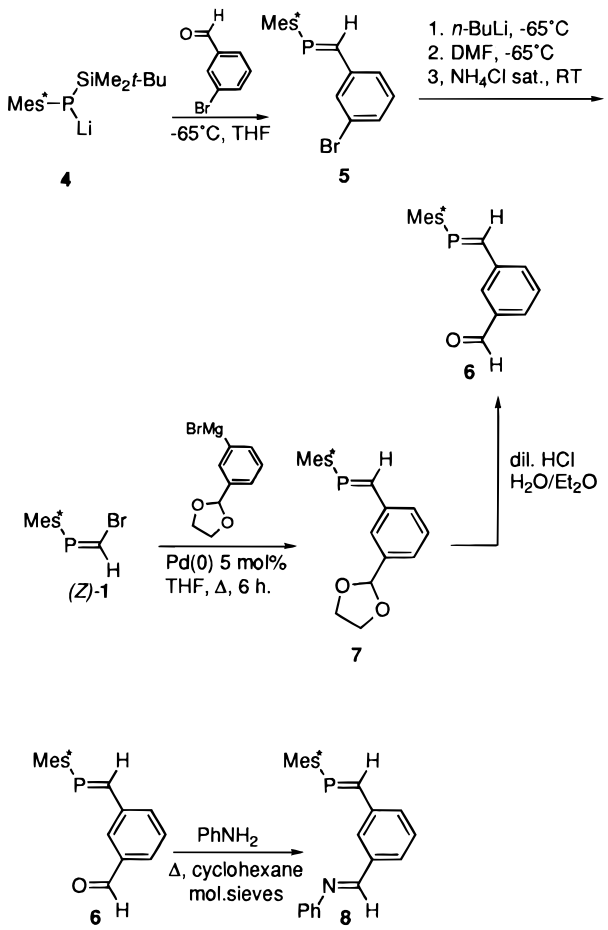
Here we present the application of this cross-coupling reaction for the preparation of two potentially bidentate ligands in which the two coordination sites are farther apart: 3-(2-pyridyl)-phosphastyrene (**2**) and 3-(*N*-phenylcarbaldimino)phosphastyrene (**8**). We also describe the unique reactivity of these two phosphaalkenes with MePdCl(COD) which unexpectedly gave the three-membered phosphapalladacycles **10** and **9**, respectively, by a novel insertion of the P═C bond into a palladium−carbon bond.

Synthesis

During our investigations on new methods for the preparation of functionalized phosphaalkenes, we recently developed a versatile Pd(0)-catalyzed cross-coupling reaction of (*Z*)-**1** with aryl Grignard reagents, furnishing a variety of novel functionalized 2-phosphastyrenes in high yield and 100% isomeric purity. This reaction has the same overall result as conventional Stille-type coupling reactions but has a different mechanistic course: it occurs with inversion of configuration and was therefore proposed to proceed through an η^2-palladium complex such as **3**, which reacts with the Grignard reagent under nucleophilic substitution of bromine; the intermediate **3** was identified by NMR spectroscopy.[5c] By the same procedure, (*Z*)-**1** was converted into the 3-(2-pyridyl)-2-phosphastyrene **2** by cross-coupling with the Grignard reagent prepared from 1-bromo-3-(2-pyridyl)benzene. The product (*Z*)-**2** was isolated in 71% yield as an air-stable crystalline solid (Scheme 1).

For the preparation of ligand **8**, two less direct routes were developed. The first route starts with bromophosphastyrene **5**, obtained by the "classical" approach which

Scheme 2



had similarly been applied by Yoshifuji et al.[2a,b,d] and Geoffroy et al.:[1] lithium phosphide **4** was reacted with 3-bromobenzaldehyde at −65 °C, furnishing **5** in 82% yield (Scheme 2). Product **5** was lithiated by a bromine−lithium exchange reaction with *n*-butyllithium at −65 °C. The addition of dimethylformamide and subsequent hydrolysis at room temperature furnished **6** as the only product in 62% yield. The second route proceeds via the dioxolane derivative **7**, a "protected" form of **6**.[10] The Grignard reagent prepared from 2-(3-bromophenyl)-1,3-dioxolane and magnesium in THF was reacted with (*Z*)-**1** under the standard coupling conditions. After workup, **7** was isolated in 62% yield as yellow crystals. For the conversion of a dioxolane into an aldehyde, a variety of mild reagents are known.[10] However, quite unexpectedly, harsh deprotection with hydrochloric acid appeared to be the most convenient way. Although phosphaalkenes generally react by addition of HCl to the P═C double bond,[11] stirring **7** overnight in a mixture of diethyl ether and dilute hydrochloric acid at ambient temperature furnished **6** in 57% yield.

Finally, **8** was prepared by heating **6** with aniline in the presence of molecular sieves in cyclohexane under reflux (Scheme 2). The condensation was monitored by ^{31}P NMR spectroscopy and was found to be complete after 1.5 h. Removal of the molecular sieves, evaporation

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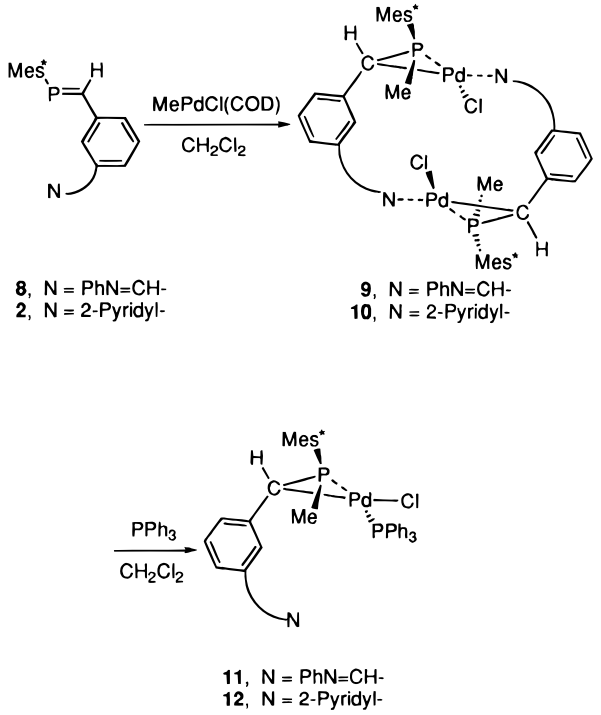
Scheme 3



of the solvent, and crystallization conveniently furnished **8** in 95% yield.

Coordination Chemistry of 2 and 8

Compounds **2** and **8** were reacted with MePdCl(COD) in dichloromethane at ambient temperature for 5 min (Scheme 3). Unexpectedly, we isolated *not* the straightforward mono- or bidentate complexes in which the phosphaalkene is coordinated via phosphorus in a η^1-fashion to palladium, but the remarkable dimeric palladium(II) complexes **10** and **9**, respectively, which contain a three-membered ring involving palladium, phosphorus, and carbon. This follows from their spectroscopic data and was, in the case of **10**, confirmed by an X-ray crystal structure determination (vide infra).

The ^{31}P NMR spectra of **9** and **10** both show a characteristic signal at $\delta(^{31}P)$ −34 in $CDCl_3$. This indicates the conversion of the phosphaalkene moiety (typical ^{31}P NMR range 200−300 ppm) to a trivalent σ^3,λ^3-phosphine. The ^{1}H NMR spectra of **9** and **10** show a signal for one proton at $\delta(^1H)$ 3.10 (in $CDCl_3$) and 3.38, respectively, which suggests the presence of one benzylic proton. One methyl group gave doublets at $\delta(^1H)$ 2.19 and 2.01 (in $CDCl_3$), respectively, with coupling constants ^2J = 12.0 and 11.3 Hz, respectively, which are characteristic for a P−Me moiety.

Presumably, after the usual initial η^1-coordination of these phosphaalkenes to methylpalladium chloride, an insertion of the P=C bond into the palladium−methyl bond occurred or, put in a different way, an addition of the palladium−carbon bond to the P=C double bond or carbapalladation. The mechanism of this reaction is unknown; it may be analogous to the initial step in the thoroughly studied Heck reaction.[12] Next, the phosphorus lone pair forms a chelate bond to palladium. Whatever the exact mechanism may be, its regiochemistry is in line with that of the addition of organometallic reagents to P=C bonds in general. Due to the electronegativity x of the two elements involved (x(P) = 2.1, x(C) = 2.5), the polarization of this bond is $^{\delta+}$P=C$^{\delta-}$; consequently, the carbanion equivalent adds to phosphorus and the metal adds to carbon. In contrast, the C=N bonds of imines possess the opposite polarization (x(N) = 3.0) and therefore show the opposite regiochemistry in analogous additions; similarly, nitriles R−C≡N have recently been reported to insert into the Ar−Pd bond to furnish palladaimines Ar(R)C=N−Pd.[13]

The addition of triphenylphosphine to **9** and **10** in dichloromethane at room temperature leads to rupture of the Pd−N bonds interconnecting the two units and replaces them by the stronger Ph_3P−Pd bonds to furnish monomeric **11** and **12** in 80% and 67% yields, respectively (Scheme 3); they were identified by their spectral data. As the crystal structure of **10** shows it to be a mixture of two enantiomers (*RS* and *SR*), this probably holds for **11** and **12** as well. In both compounds, the ^{31}P NMR spectrum shows a double doublet with absorptions at δ 22 and −39 (J(PP) = 393−397 Hz). The characteristic ^{31}P chemical shift at δ −39 signals that the three-membered palladacycle has been retained. The large J(PP) value clearly indicates that in **11** and **12** the phosphorus ligands at palladium are trans. In the case of **12**, the chemical shift of the pyridine *ortho* proton ($\delta(^1H)$ 8.66) shows that the pyridine ring is noncoordinating; on coordination, this proton becomes more deshielded, as illustrated by the value $\delta(^1H)$ 9.05 in **10**.

X-ray Crystal Structure Determination of 10

The structure of **10** shows a dimer located on a crystallographic inversion center (point-symmetric and dimeric); it contains two enantiomeric (*RS* and *SR*) 3-(2-pyridyl)-1-[(supermesityl)(methyl)-η^1-phosphino-σ-methyl]benzene palladium chloride(II) units wherein the σ-bonding ligands, C(1) and Cl(1), are fixed in a *cis* arrangement around the square-planar palladium center. The benzylic carbon atom C(1) is σ-bonded to palladium, and the phosphorus atom P(1) is η^1-coordinated to palladium; thus, a three-membered palladacycle is formed by intramolecular coordination. The pyridine moiety of one unit coordinates to the palladium center of the other one, which leads to the dimeric structure (Figure 1, Tables 1 and 2). The asymmetric unit contains four chloroform molecules, three of which display a short C−H···Cl interaction with the Pd−Cl moiety.

The C(2)−P(1)−C(1)−C(3) moiety is planar with a torsion angle of −0.8(9)°, and the H(1)−C(1)−P(1)−C(14) moiety has a torsion angle of −11.4(8)°. The P(1)−Pd(1)−C(1) angle (48.0(2)°) is very small compared to the optimal angle of 90° for a square-planar palladium complex but is comparable to that of $(Me_3P)_2$-Ni[$(Me_3Si)_2$CPC(H)($SiMe_3$)$_2$] (P−Ni−C = 48.9(2)°).[14] This small angle is mainly compensated by the large P(1)−Pd(1)−N(1)^a angle (122.92(16)°).

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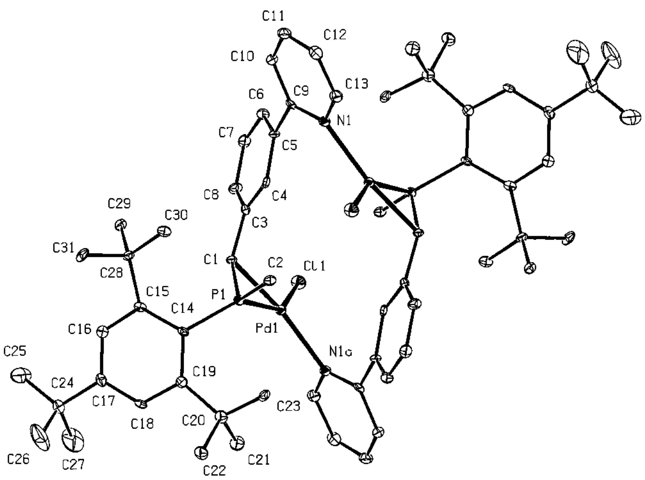

Figure 1. ORTEP[24] drawing (30% probability level) of **10**. Hydrogen atoms and coordinating chloroform molecules have been omitted for clarity.

Table 1. Crystallographic Data for 10

Crystal Data	
formula	$C_{62}H_{82}Cl_2N_2P_2Pd_2 \cdot 8CHCl_3$
mol wt	2156.06
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a, Å	13.6333(17)
b, Å	18.674(3)
c, Å	18.330(3)
β, deg	97.998(12)
V, Å^3	4621.2(12)
D_{calcd}, g cm^{-3}	1.549
Z	2
F(000)	2176
μ, cm^{-1}	12.1
cryst size, mm	0.2 × 0.2 × 0.3
Data Collection	
T, K	150
θ_{min}, θ_{max}, deg	1.09, 25.00
wavelength (Mo Kα), Å	0.710 73 (graphite monochromator)
scan type	ω
$\Delta\omega$, deg	0.67 + 0.35 tan θ
horiz, vert aperture, mm	3.00 + 1.50 tan θ, 4.00
X-ray exposure time, h	91
linear decay, %	7
ref rflns	$\bar{2}\,\bar{4}1$, $4\bar{2}3$, $\bar{2}\bar{6}2$
data set (hkl)	−16 to +16, −22 to 0, −21 to +21
total no. of data	16 009
total no. of unique data	8142 (R_{int} = 0.108)
Refinement	
no. of refined params	470
wR2[a]	0.1450
R[b]	0.0655 (for 4313 $F_o > 4\sigma(F_o)$)
S	1.016
w^{-1} [c]	$\sigma^2(F^2) + (0.0500P)^2$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.000, 0.006
min and max resid density, e Å^{-3}	−0.71, 0.72

[a] wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $P = (\mathrm{Max}(F_o^2, 0) + 2F_o^2)/3$.

The Pd(1)−N(1)[a] bond length is 2.168(6) Å, which is comparable to that in [Mes*P=C(SiMe$_3$)Py]MePdCl (2.164(4) Å).[5d] The Pd(1)−Cl(1) bond length is 2.411(2) Å, which is considerably longer than that in [Mes*P=C(SiMe$_3$)Py]MePdCl (2.3545(14) Å) or in the phosphine complex (PAN)MePdCl (2.3869(8) Å; PAN = 1-(dimethylamino)-8-(diphenylphosphino)naphthalene).[15] The P(1)−C(1) bond length is 1.754(8) Å, which is smaller than but comparable to that in $(Me_3P)_2Ni[(Me_3Si)_2C{-}PC(H)(SiMe_3)_2]$[14] ($d$(P−C) = 1.773(8) Å). A "normal" η^1-P(sp^3)−C(sp^3) bond length is 1.82 Å, which is considerably longer.[14] Finally, the P(1)−Pd(1) bond length is 2.2217(19) Å, which is comparable to that in (PAN)MePdCl (2.2009(8) Å).[15]

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for 10 (Esds in Parentheses)

Bond Lengths			
P(1)−C(1)	1.754(8)	Pd(1)−Cl(1)	2.411(2)
P(1)−Pd(1)	2.2217(19)	Pd(1)−C(14)	1.841(8)
C(1)−Pd(1)	2.081(8)	C(1)−C(3)	1.498(11)
Pd(1)−N(1)[a]	2.168(6)	C(5)−C(9)	1.464(11)
Bond Angles and Torsion Angles			
P(1)−Pd(1)−C(1)	48.0(2)	P(1)−C(1)−C(3)	132.9(6)
P(1)−C(1)−Pd(1)	70.2(3)	C(9)−N(1)−C(13)	119.4(6)
C(1)−Pd(1)−Cl(1)	99.2(2)	P(1)−C(1)−Pd(1)−Cl(1)	179.2(2)
C(1)−P(1)−Pd(1)	61.8(2)	C(1)−P(1)−Pd(1)−N(1)[a]	−174.6(4)
Cl(1)−Pd(1)−N(1)[a]	89.73(16)	C(3)−C(1)−P(1)−C(14)	134.7(7)
P(1)−Pd(1)−N(1)[a]	122.92(16)	C(2)−P(1)−C(1)−C(3)	−0.8(9)
C(1)−P(1)−C(14)	108.6(4)	H(1)−C(1)−P(1)−C(14)	−11.4(8)
C(1)−P(1)−C(2)	117.4(4)	P(1)−C(1)−C(3)−C(4)	−4.8(12)
C(2)−P(1)−Pd(1)	117.7(2)	H(1)−C(1)−C(3)−C(8)	−36.3(10)
Pd(1)−P(1)−C(14)	121.2(2)	C(1)−P(1)−C(14)−C(15)	−34.4(7)
C(2)−P(1)−C(14)	117.0(3)	C(6)−C(5)−C(9)−N(1)	−143.9(7)

[a] Indicates symmetry operation 2 − x, 1 − y, −z.

Three-membered metallacycles of the type $R_2\overline{P{-}CH_2{-}M}$ are well-established. They have been isolated for several metals and have been prepared by a variety of methods.[16] However, only few examples of the preparation of these species from phosphaalkenes are known. Recently, Majoral et al. described the hydrozirconation of phosphaalkenes leading to phosphazirconacyclopropanes.[17] Geoffroy et al. reported the formation and X-ray crystal structure of a phosphapalladacyclopropane by reacting a phosphaalkene−$PdCl_2$ complex with alcohols.[1e] Our carbapalladation of the P=C double bond opens a novel approach to such species.

Experimental Section

All experiments were performed in oven-dried glassware and under nitrogen. Solvents were distilled from sodium benzophenone (THF), lithium aluminum hydride (pentane, diethyl ether), or calcium chloride (dichloromethane). All solid starting materials were dried in vacuo. Liquids were distilled under N_2 prior to use. NMR spectra were recorded with a Bruker AC 200 (^{1}H, ^{13}C (50.32 MHz)) and Bruker MSL 400 spectrometers (^{1}H, ^{13}C (100.63 MHz), variable-temperature ^{31}P (162.00 MHz)) or with a Bruker WM 250 spectrometer (^{31}P (101.25 MHz)). Tetramethylsilane (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P) was used as an external standard. Mass spectra were recorded with a Finnigan MAT 90 spectrometer; accurate masses were determined by peak matching at a mass resolution of approximately 10 000. Elemental analyses were performed by

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Microanalytisches Labor Pascher, Remagen, Germany. Compounds (*Z*)-**1**,[5c] **4**,[2] and MePdCl(COD)[18] were prepared according to literature procedures.

(*E*)-((3-Bromophenyl)methylene)(2,4,6-tri-*tert*-butylphenyl)phosphine (5). 3-Bromobenzaldehyde (0.43 g, 2.33 mmol) was dropped into a solution of **4** (2.33 mmol) in THF (10 mL) at −65 °C. The reaction mixture was warmed to room temperature, after which trimethylsilyl chloride (0.26 g, 2.36 mmol) was added. The solvent was evaporated, and the orange residue was dissolved in pentane. This solution was flushed through a silica column. The pentane was evaporated under reduced pressure, and the residue was crystallized from acetonitrile, furnishing **5** as white crystals (yield 0.85 g, 1.91 mmol, 82%); mp 116−118 °C. ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 9H, *p*-*t*-Bu), 1.49 (s, 18H, *o*-*t*-Bu), 7.14 (m, 1H), 7.32 (m, 1H), 7.43 [d, 2H, ^4J(HP) = 1.3 Hz, Ar *H*], 7.68 (m, 1H), 7.99 [d, 1H, ^2J(HP) = 25.4 Hz, P=C*H*]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 31.3 [s, *p*-C(CH_3)$_3$], 33.7 [d, ^4J(CP) = 7.0 Hz, *o*-C(CH_3)$_3$], 34.9 [s, *p*-*C*(CH_3)$_3$], 38.1 [s, *o*-*C*(CH_3)$_3$], 121.7 (s, *m*-Ar), 119.3−142.1 (aromatic C), 149.8 (s, *o*-Ar), 153.9 (s, *p*-Ar), 173.5 [d, ^1J(CP) = 35.2 Hz, P=*C*]. ^{31}P NMR ($CDCl_3$): δ 269. MS (70 eV): *m*/*z* (%) 444 (4) [M^+], 387 (1) [M^+ − *t*-Bu]. HRMS: calcd for $C_{25}H_{34}P_{79}Br$ 444.1582, found 444.1582. Anal. Calcd for $C_{25}H_{34}$PBr: C, 67.41; H, 7.70. Found: C, 67.38; H, 7.61.

(*E*)-((3-(1,3-Dioxol-2-yl)phenyl)methylene)(2,4,6-tri-*tert*-butylphenyl)phosphine (7). A solution of the Grignard reagent, prepared by stirring 2-(3-bromophenyl)-1,3-dioxolane (2.29 g, 10 mmol) with magnesium (0.48 g, 20 mmol) in THF (20 mL), was dropped into a solution of (*Z*)-**1** (1.44 g, 4 mmol), tetrakis(triphenylphosphine)palladium(0) (5 mol %, prepared in situ from $Pd_2(dba)_3$ (0.092 g, 0.1 mmol; dba = dibenzylideneacetone), and triphenylphosphine (0.209 g, 0.8 mmol)) in THF (5 mL). The reaction mixture was heated under reflux for 6 h, after which the solvent was removed under reduced pressure. The residue was added to the top of a small silica column, which was flushed with dichloromethane. Evaporation of the dichloromethane furnished a yellow solid. Crystallization of the product from hot acetonitrile furnished yellow crystals (yield 1.09 g, 2.48 mmol, 62%); mp 148−150 °C. ^{1}H NMR ($CDCl_3$): δ 1.40 (s, 9H, *p*-*t*-Bu), 1.56 (s, 18H, *o*-*t*-Bu), 4.00−4.21 (m, 4H, dioxolane CH_2), 5.82 (s, 1H, dioxolane C*H*), 7.33 (m, 2H), 7.49 [d, 2H, ^4J(HP) = 1.0 Hz, Ar *H*], 7.58−7.70 (m, 2H), 8.16 [d, 1H, ^2J(HP) = 25.5 Hz, P=C*H*]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 31.3 [s, *p*-C(CH_3)$_3$], 33.7 [d, ^4J(CP) = 7.1 Hz, *o*-C(CH_3)$_3$], 34.9 [s, *p*-*C*(CH_3)$_3$], 38.2 [s, *o*-*C*(CH_3)$_3$], 65.2 (s, dioxolane *C*H_2), 103.5 (s, dioxolane *C*H), 121.7 (s, *m*-Ar), 123.5−140.3 (aromatic C), 149.6 (s, *o*-Ar), 153.9 (s, *p*-Ar), 175.3 [d, ^1J(CP) = 34.6 Hz, P=*C*]. ^{31}P NMR ($CDCl_3$): δ = 262. MS (70 eV): *m*/*z* (%) 438 (22) [M^+], 381 (2) [M^+ − *t*-Bu]. HRMS: calcd for $C_{28}H_{39}O_2P$ 438.2688, found 438.2687. Anal. Calcd for $C_{28}H_{39}O_2P$: C, 76.67; H, 8.97; O, 7.30. Found: C, 76.41; H, 8.96; O, 7.13.

(*E*)-((3-Formylphenyl)methylene)(2,4,6-tri-*tert*-butylphenyl)phosphine (6). From 5. Phosphaalkene **5** (4.23 g, 9.49 mmol) was dissolved in THF (50 mL) and the solution cooled to −65 °C. At −65 °C a solution of *n*-butyllithium in hexane (6.25 mL, 1.6 M, 10 mmol) was added, furnishing a red suspension. After the reaction mixture was stirred for 15 min at the same temperature, dimethylformamide (0.73 g, 9.99 mmol) was added. The mixture was warmed to room temperature, after which a saturated solution of ammonium chloride in water was added. The solvent was evaporated, and the residue was extracted with pentane. After the pentane layer was dried with magnesium sulfate and filtered, the pentane was evaporated from the filtrate under reduced pressure, furnishing a white solid. Crystallization of the product from *n*-hexane furnished **6** (yield 2.30 g, 5.83 mmol, 62%). The spectral data were identical with those of **6** prepared as described below.

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From 7. To a solution of **7** (0.80 g, 1.82 mmol) in diethyl ether (30 mL) was added dilute HCl in water (2.5 M, 10 mL). The mixture was vigorously stirred overnight. The ether layer was separated, dried over magnesium sulfate, and filtered. The solvent was evaporated under reduced pressure, furnishing a yellowish oil which solidified on standing. Crystallization of the product from *n*-hexane furnished **6** (yield 0.41 g, 1.04 mmol, 57%); mp 90−92 °C. ^{1}H NMR ($CDCl_3$): δ 1.26 (s, 9H, *p*-*t*-Bu), 1.42 (s, 18H, *o*-*t*-Bu), 7.35 [d, 2H, ^4J(HP) = 1.3 Hz, Ar *H*], 7.36 (m, 1H), 7.65 (m, 2H), 7.92 (m, 1H), 8.04 [d, 1H, ^2J(HP) = 25.3 Hz, P=C*H*], 9.92 (s, 1H, O=C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 31.4 [s, *p*-C(CH_3)$_3$], 33.9 [d, ^4J(CP) = 6.9 Hz, *o*-C(CH_3)$_3$], 35.0 [s, *p*-*C*(CH_3)$_3$], 38.2 [s, *o*-*C*(CH_3)$_3$], 121.9 (s, *m*-Ar), 126.8−131.2 (aromatic C), 138.2 [d, ^1J(CP) = 53.2 Hz, *ipso*-Ar], 140.8 [d, *J*(CP) = 14.6 Hz], 149.9 (s, *o*-Ar), 154.0 (s, *p*-Ar), 173.7 [d, ^1J(CP) = 35.2 Hz, P=*C*], 191.9 (s, *C*=O). ^{31}P NMR ($CDCl_3$): δ 270. MS (70 eV): *m*/*z* (%) 494 (5) [M^+], 337 (3) [M^+ − *t*-Bu]. HRMS: calcd for $C_{26}H_{35}OP$ 394.2426, found 394.2426. Anal. Calcd for $C_{26}H_{35}OP$: C, 79.15; H, 8.95. Found: C, 78.63; H, 9.53.

(*E*)-((3-(*N*-Phenylcarbaldimino)phenyl)methylene)-(2,4,6-tri-*tert*-butylphenyl)phosphine (8). Phosphaalkene **6** (2.29 g, 5.80 mmol) and aniline (0.65 mL, 7.0 mmol) were dissolved in cyclohexane (25 mL). After the addition of molecular sieves (1.5 g; 8−12 mesh, 3 Å), the reaction mixture was heated under reflux for 1.5 h. The solution was filtered, and the solvent was evaporated under reduced pressure. The residue was crystallized from *n*-hexane, furnishing **8** as a white solid (yield 2.58 g, 5.51 mmol, 95%); mp 118−120 °C. ^{1}H NMR ($CDCl_3$): δ 1.29 (s, 9H, *p*-*t*-Bu), 1.46 (s, 18H, *o*-*t*-Bu), 7.13 (m, 3H), 7.31 (m, 3H), 7.38 [d, 2H, ^4J(HP) = 1.2 Hz, Ar *H*], 7.65 (m, 1H), 7.85 (m, 1H), 8.09 [d, 1H, ^2J(HP) = 25.4 Hz, P=C*H*], 8.39 (s, 1H, N=C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 31.4 [s, *p*-C(CH_3)$_3$], 33.9 [d, ^4J(CP) = 7.0 Hz, *o*-C(CH_3)$_3$], 35.0 [s, *p*-*C*(CH_3)$_3$], 38.3 [s, *o*-*C*(CH_3)$_3$], 120.9−129.1 (aromatic C), 121.8 (s, *m*-Ar), 136.7 [d, *J*(CP) = 2.5 Hz], 138.7 [d, ^1J(CP) = 53.3 Hz, *ipso*-Ar], 140.9 [d, *J*(CP) = 13.9 Hz], 149.7 (s, *o*-Ar), 154.0 (s, *p*-Ar), 160.0 (s, N=*C*), 174.9 [d, ^1J(CP) = 35.7 Hz, P=*C*]. ^{31}P NMR ($CDCl_3$): δ 265. MS (70 eV): *m*/*z* (%) 469 (12) [M^+], 412 (4) [M^+ − *t*-Bu]. HRMS: calcd for $C_{32}H_{40}NP$ 469.2898, found 469.2898. Anal. Calcd for $C_{32}H_{40}NP$: C, 81.83; H, 8.59. Found: C, 81.14; H, 9.19.

3-(2-Pyridyl)bromobenzene. To a solution of 2-(trimethylstannyl)pyridine (13.3 g, 55.0 mmol) in toluene (500 mL) was added 1-bromo-3-iodobenzene (15.7 g, 55.0 mmol) and tetrakis(triphenylphosphine)palladium(0) (5 mol %, 3.2 g, 2.75 mmol). The mixture was heated under reflux overnight, and the progress of the reaction was monitored by GC-MS. The crude product was separated from the reaction mixture by extraction with hydrochloric acid. The aqueous layer was neutralized with sodium hydroxide and then extracted with diethyl ether. The solvent was evaporated and the product distilled under vacuum (4 mmHg, 131 °C), furnishing the pure bromide (yield 9.3 g, 39.7 mmol, 72%). ^{1}H NMR ($CDCl_3$): δ 7.15 [t, 1H, *J*(HH) = 4.9 Hz], 7.24 [t, 1H, *J*(HH) = 7.9 Hz], 7.46 [d, 1H, *J*(HH) = 8.0 Hz], 7.60 [t, 1H, *J*(HH) = 8.5 Hz], 7.64 [t, 1H, *J*(HH) = 8.9 Hz], 7.83 [d, 1H, *J*(HH) = 7.7 Hz], 8.13 (s, 1H), 8.62 [d, 1H, *J*(HH) = 4.6 Hz]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 120.5 (s), 125.5 (s), 125.2 (s), 129.8 (s), 130.1 (s), 136.7 (s), 149.6 (s), 155.5 (s). MS (70 eV): *m*/*z* (%) 233 (84) [M^+], 154 (100) [M^+ − Br]. HRMS: calcd for $C_{11}H_8N_{79}Br$ 232.9840, found 232.9845.

(*E*)-((3-(2-Pyridyl)phenyl)methylene)(2,4,6-tri-*tert*-butylphenyl)phosphine (2). The Grignard reagent prepared from 3-(2-pyridyl)bromobenzene (0.94 g, 4 mmol) and magnesium (0.19 g, 8 mmol) in THF was added to a solution of (*Z*)-**1** (0.72 g, 2 mmol) and tetrakis(triphenylphosphine)palladium-(0) (5 mol %), prepared in situ from $Pd_2(dba)_3$ (0.046 g) and triphenylphosphine (0.10 g), in THF (5 mL). The reaction mixture was heated under reflux for 6 h. The solvent was evaporated, and the residue was flushed over a silica column: first with pentane, which removes the organic byproducts, and

then with diethyl ether, which removes the product. The product was crystallized from hot acetonitrile, furnishing **2** (yield 0.63 g, 1.42 mmol, 71%); mp 157−158 °C. ^{1}H NMR ($CDCl_3$): δ 1.35 (s, 9H, *p*-*t*-Bu), 1.52 (s, 18H, *o*-*t*-Bu), 7.23 (m, 1H), 7.38 (m, 1H), 7.45 (s, 2H, Ar *H*), 7.63−7.88 (m, 4H), 8.12 (s, 1H, *o*-Ph *H*), 8.18 [d, 1H, ^2J(HP) = 25.5 Hz, P═C*H*], 8.79 (m, 1H, *o*-Py *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 31.3 [s, *p*-C(*C*H_3)$_3$], 33.7 [d, ^4J(CP) = 7.0 Hz, *o*-C(*C*H_3)$_3$], 34.9 [s, *p*-*C*(CH_3)$_3$], 38.1 [s, *o*-*C*(CH_3)$_3$], 120.6−157.0 (pyridyl and aromatic C), 121.7 (s, *m*-Ar), 140.9 [d, *J*(CP) = 13.9 Hz], 149.5 [d, ^2J(CP) = 4.6 Hz, *o*-Ar], 154.0 (s, *p*-Ar), 175.5 [d, ^1J(CP) = 34.6 Hz, P═*C*]. ^{31}P NMR ($CDCl_3$): δ 258. MS (70 eV): *m*/*z* (%) 443 (12) [M^+], 386 (6) [M^+ − *t*-Bu]. HRMS: calcd for $C_{30}H_{38}NP$ 443.2742, found 443.2740. Anal. Calcd for $C_{30}H_{38}NP$: C, 81.22; H, 8.64; N, 3.16. Found: C, 80.83; H, 8.61; N, 3.15.

General Procedure for the Preparation of 9 and 10. Ligand **8** (0.23 g, 0.5 mmol) or **2** (0.22 g, 0.5 mmol), respectively, was mixed with MePdCl(COD) (0.13 g, 0.5 mmol) and dissolved in dichloromethane (5 mL). The yellow-orange solution was stirred for 5 min at ambient temperature. The solvent was evaporated, and the yellow residue was washed with pentane (5 mL). The yellow product was dried under vacuum, furnishing **9** and **10**, respectively.

9: yield 0.23 g, 0.36 mmol, 71%; mp 183−185 °C. ^{1}H NMR ($CDCl_3$): [δ 1.28 (s) and 1.31 (d, *J* = 2.5 Hz), 18H, *o*-*t*-Bu], [1.58 (br s) and 1.75 (br s), 9H, *p*-*t*-Bu], 2.19 [d, 3H, ^2J(HP) = 12.0 Hz, P−Me], 3.10 (1H, P−C*H*), 7.20−7.76 (m, Ar *H*), 8.39 (s, 1H, N═C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 17.2 (P−Me), 31.0−34.7 (*p*-*t*-Bu and *o*-*t*-Bu), 39.9 (s, *C*H), 115−155 (aromatic C). ^{31}P NMR ($CDCl_3$): δ −33.8 and −34.4. MS (EI, 70 eV): *m*/*z* (%) 627 (12.6) [M^+], 591 (50.6) [M^+ − Cl], 575 (6.5) [M^+ − Cl − CH_4]. HRMS: calcd for $C_{33}H_{43}NP^{105}Pd^{35}Cl$ 624.1868, found 624.1860. Anal. Calcd for $C_{33}H_{43}NPPdCl$: C, 63.26; H, 6.92; Pd, 16.9. Found: C, 62.67; H, 7.26; Pd, 16.9.

10: yield 0.27 g, 0.45 mmol, 90%; mp 179−181 °C. ^{1}H NMR ($CDCl_3$): δ 0.97 (9H, *o*-*t*-Bu), 1.15 (9H, *o*-*t*-Bu), 1.22 (s, 9H, *p*-*t*-Bu), 2.01 [d, 3H, ^2J(HP) = 11.3 Hz, P−Me], 3.38 (1H, P−C*H*), 7.02 (m, 1H), 7.38 (s, 2H, Ar *H*), 7.60 (m, 1H), 7.71 (m, 3H), 8.44 (s, 1H, *o*-Ph *H*), 9.05 [d, 1H, ^3J(HH) = 5.5 Hz, *o*-Py *H*]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 17.5 [d, ^1J(CP) = 21.0 Hz, P−Me], 30.8 [s, *p*-C(*C*H_3)$_3$], 33.6 [d, *o*-C(*C*H_3)$_3$, *J*(CP) = 8.3 Hz], 34.4 [s, *p*−*C*(CH_3)$_3$], 38.9 [d, *o*-*C*(CH_3)$_3$, *J*(CP) = 3.5 Hz], 40.3 (s, *C*H), 118.1−160.7 [pyridyl and aromatic C]. ^{31}P NMR ($CDCl_3$): δ −34. MS (EI, 70 eV): *m*/*z* (%) 601 (0.8) [M^+], 565 (2.1) [M^+ − Cl], 549 (0.2) [M^+ − Cl − CH_4]. HRMS: calcd for $C_{31}H_{41}NP^{104}Pd^{35}Cl$ 597.1701, found 597.1694. Anal. Calcd for $C_{31}H_{41}NPPdCl$: C, 62.00; H, 6.89; Pd, 17.7. Found: C, 61.86; H, 7.18; Pd, 17.5.

General Procedure for the Preparation of 11 and 12. To a solution of **9** or **10** in dichloromethane, prepared as described above, was added 1 equiv of triphenylphosphine (0.13 g, 0.5 mmol). The solution was stirred for 10 min at ambient temperature. After filtration the solvent was evaporated and the yellow residue was washed with pentane (5 mL). The yellow residue was dried under vacuum, furnishing **11** and **12**, respectively.

11: yield 0.36 g, 0.40 mmol, 80%; mp 91−93 °C. ^{1}H NMR ($CDCl_3$): δ 1.32 (s, 18H, *o*-*t*-Bu), 1.90 (s, 9H, *p*-*t*-Bu), 2.25 [dd, 3H, ^2J(HP) = 10.8 Hz, ^4J(HP) = 3.9 Hz, P−Me], 2.63 [d, 1H, ^2J(HP) = 4.6 Hz, P−C*H*], 6.66−7.58 (m, aromatic H), 8.15 (s, 1H, N═C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 16.0 (dd, P−Me), 30.8 [s, *p*-C(*C*H_3)$_3$], 33.9 [d, *o*-C(*C*H_3)$_3$, *J*(CP) = 14.8 Hz], 34.6 [s, *p*-*C*(CH_3)$_3$], 39.9 [d, *o*-*C*(CH_3)$_3$, *J*(CP) = 15.14 Hz], 44.0 (dd, *C*H), 120.7−151.8 (aromatic C), 159.8 (s, N═*C*). ^{31}P NMR ($CDCl_3$): δ 22 (d, ^2J(PP) = 397 Hz, PPh_3), −39 [d, ^2J(PP) = 397 Hz, Mes*PMe]. MS (EI, 70 eV): *m*/*z* (%) 889 (1.38) [M^+], 853 (0.59) [M^+ − Cl], 591 (1.9) [M^+ − Cl − PPh_3]. Anal. Calcd for $C_{51}H_{58}NP_2ClPd$: C, 68.91; H, 6.58; Pd, 12.0. Found: C, 67.97; H, 6.82; Pd, 12.1.

12: yield 0.29 g, 0.33 mmol, 67%; mp 110−113 °C. ^{1}H NMR ($CDCl_3$): δ 1.32 (s, 18H, *o*-*t*-Bu), 1.90 (s, 9H, *p*-*t*-Bu), 2.26 [dd, 3H, ^2J(HP) = 10.9 Hz, ^4J(HP) = 4.0 Hz, P−Me], 2.64 (d, 1H, ^2J(HP) = 5.0 Hz, P−C*H*), 6.74 (m, 1H), 6.91−7.76 (m, aromatic H), 8.66 [d, 1H, ^3J(HH) = 4.0 Hz, *o*-Py *H*]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 15.1 [dd, ^1J(CP) = 14.8 Hz, ^3J(CP) = 8.3 Hz, P−Me], 31.9 [s, *p*-C(*C*H_3)$_3$], 34.4 [d, *o*-C(*C*H_3)$_3$, *J*(CP) = 27.7 Hz], 34.7 [s, *p*-*C*(CH_3)$_3$], 39.9 [d, *o*-*C*(CH_3)$_3$, *J*(CP) = 10.1 Hz], 43.7 [d, ^1J(CP) = 23.2 Hz, *C*H], 117.6−161.0 (pyridyl and aromatic C). ^{31}P NMR ($CDCl_3$): δ 22 (d, ^2J(PP) = 393 Hz, PPh_3), −39 (d, ^2J(PP) = 393 Hz, Mes*PMe). MS (EI, 70 eV): *m*/*z* (%) 863 (0.17) [M^+], 827 (0.01) [M^+ − Cl], 601 (2.9) [M^+ − PPh_3].

Crystal Structure Determination and Refinement of 10. A yellow, block-shaped crystal was glued to the tip of a glass fiber and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-Turbo diffractometer on a rotating anode. Accurate unit-cell parameters and an orientation matrix were determined by least-squares fitting of the setting angles of 25 well-centered reflections (SET4[19]) in the range $9.95 < \theta < 13.80°$. Reduced-cell calculations did not indicate higher lattice symmetry.[20] Crystal data and details on data collection and refinement are given in Table 1. Data were corrected for *Lp* effects and the observed linear decay, but not for absorption. The structure was solved by automated direct methods (SHELXS96[21]). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-96[22]); no observance criterion was applied during refinement. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic displacement parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms by a factor of 1.5 for the methyl hydrogen atoms and 1.2 for the other hydrogen atoms, respectively. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 23. Geometrical calculations and illustrations were performed with PLATON.[24] All calculations were performed on a DECstation 5000/125.

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Supporting Information Available: Figures giving ^{1}H, ^{13}C, and ^{31}P NMR spectra for **11** and **12** and tables of crystal data and refinement details, positional and thermal parameters, and bond distances and angles for **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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