Synthesis of 2-(2-Pyridyl)phosphaalkenes [Mes*P=C(R)Py] (R = H, $SiMe_3$) and Their Complexes η^1,η^1-[Mes*P=C(R)Py]XPdCl (X = Cl, Me, Ac)†

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Bidentate ligands of the type Mes*P=C(R)Py (*(E)*-**2**, R = H; *(Z)*-**9**, R = $SiMe_3$; Mes* = supermesityl = 2,4,6-tri-*tert*-butylphenyl; Py = 2-pyridyl) were synthesized. Ligand *(E)*-**2** was synthesized by reacting Mes*P(Li)$SiMe_2$(*t*-Bu) (**4**) with 2-pyridinecarboxaldehyde. Ligand *(Z)*-**9** was synthesized via a $PdCl_2$(dppb)-catalyzed coupling reaction between 2-bromopyridine and Mes*P=C($SiMe_3$)M (*(E)*-**7**, M = ZnCl; *(Z)*-**8**, M = MgBr). Compound *(E)*-**2** was also characterized by an X-ray crystal structure determination; it has a planar structure with the *(E)*-configuration. The complexes η^1,η^1-[Mes*P=C(R)Py]$PdCl_2$ (**11**, R = H; **12**, R = $SiMe_3$) were prepared by the reaction of bis(benzonitrile)palladium dichloride with *(E)*-**2** and *(Z)*-**9**, respectively. The complexes η^1,η^1-[Mes*P=C(R)Py]MePdCl (**13**, R = H; **14**, R = $SiMe_3$) were obtained by a ligand exchange reaction of MePdCl(COD) with *(E)*-**2** and *(Z)*-**9**, respectively. Complex **13** was alternatively prepared by reaction of **11** with methylmagnesium chloride. Complex **14** was unambiguously identified by an X-ray crystal structure determination. Both **13** and **14** reacted with CO, resulting in the acetyl complexes η1,η1-[Mes*P=C(R)Py]AcPdCl (**16**, R = H; **17**, R = $SiMe_3$).

Introduction

Recent developments in the field of phosphaalkene- and phosphinine-based ligand systems and their complexes with metals reveal great interest in the possibly unique coordinative properties of these novel species.[1−4] This is motivated by the fact that phosphaalkenes and phosphinines are the phosphorus analogues of imines and pyridines, which are widely used in homogeneous catalysis.[5]

Several groups have recently been engaged in the synthesis of such ligand systems. Geoffroy *et al.* have been active in the field of 2-(2-pyridyl)phosphaalkenes and di(phosphaalkenyl)benzene ligands.[1] Mathey *et al.* developed phosphinine-based bidentate ligands by a Stille-type cross-coupling reaction of 2-bromophosphinines with the appropriate stannanes.[2] These investigations led to bidentate ligands which are analogues of the widely applied 2,2-bipyridine (bipy).[6] Yoshifuji *et al.* explored the field of 1,2-diphosphinidenecyclobutenes.[3d] The palladium dichloride complexes of the 1,2-diphosphinidenecyclobutenes showed catalytic activity in a Heck-type coupling reaction between trimethylsilylacetylene and *p*-bromonitrobenzene.[3d]

For some time we have been involved in the development of methodologies for the synthesis of functionalized phosphaalkenes from halogen-substituted phosphaalkenes, as the ultimate starting material.[7] Recently, we described a Pd(0)-catalyzed cross-coupling reaction of bromophosphaalkenes [*(E/Z)*-Mes*P=C(H)Br] with Grignard reagents. This has led to a variety of novel functionalized phosphaalkenes *(E)*-Mes*P=C(H)R, where R is an olefinic, (functionalized) aromatic, or heterocyclic group.[7c] The present investigations were initiated with the purpose of extending this methodology to the

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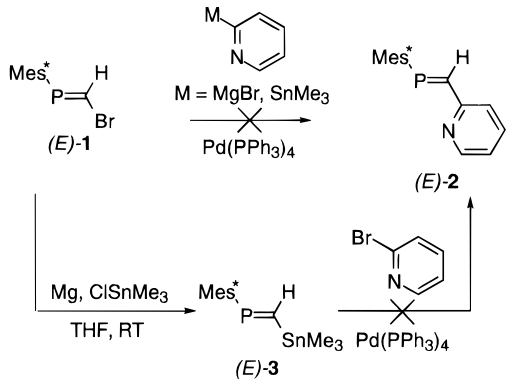
Scheme 1



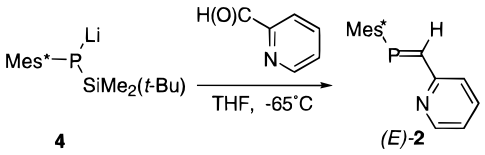
synthesis of bidentate ligands containing a phosphaalkene moiety and their complexes with transition metals.

In this paper we present our attempts to prepare 2-(2-pyridyl)phosphaalkenes of the type: Mes*P=C(R)Py (R = H, $SiMe_3$) by a palladium-catalyzed cross-coupling reaction between a phosphaalkene and a pyridine moiety and their application as bidentate ligands in novel palladium(II) complexes of the type η^1,η^1-[Mes*P=C(R)-Py]XPdCl (R = H, $SiMe_3$; X = Cl, Me, Ac). The chelating properties of the 2-(2-pyridyl)phosphaalkenes in Pd(II) complexes will be compared with those of their nitrogen analogues: the well-studied R−PyCa ligands (R−PyCa = 2-Pyridyl−C=NR).[8,9]

Results and Discussion

Synthesis of 2-(2-Pyridyl)phosphaalkenes. Recently, we described the use of a palladium(0)-catalyzed cross-coupling reaction of bromophosphaalkenes *(E/Z)*-Mes*P=C(H)Br with Grignard reagents (RMgBr), furnishing functionalized phosphaalkenes of the type *(E)*-Mes*P=C(H)R.[7c] However, the introduction of a pyridine functionality, which would furnish the bidentate ligand *(E)*-**2**, failed. Both the Grignard reagent prepared from 2-bromopyridine[10] and 2-(trimethylstannyl)pyridine[11] did not react with bromophosphaalkene *(E)*-**1** in the presence of a catalytic amount (5 mol %) of tetrakis-(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] (Scheme 1); the ^{31}P NMR spectra of the crude reaction mixture showed only the presence of starting material *(E)*-**1** in both cases. Therefore, we investigated the reverse combination by reacting *(E)*-trimethylstannylphosphaalkene *(E)*-**3** with 2-bromopyridine in the presence of Pd-$(PPh_3)_4$. Isomerically pure *(E)*-**3** was prepared by the reaction of *(E)*-**1** with magnesium and trimethylchlorostannane under Barbier conditions; this method had been applied by Mathey *et al.* for the preparation of a 2-trimethylstannylphosphinine.[2b] Presumably, trimethylchlorostannane reacts with the *in situ* prepared Grignard reagent of *(E)*-**1** to furnish *(E)*-**3**, an oil which was used without further purification. However, under a variety of conditions, a Stille coupling between *(E)*-**3** and 2-bromopyridine could not be accomplished; analysis of the reaction mixtures by ^{31}P NMR spectroscopy showed only starting material *(E)*-**3** ($\delta(^{31}P) = 322$) in all attempts (Scheme 1).

Scheme 2



So we prepared *(E)*-**2** by the "classical" approach, which had been reported earlier by Geoffroy *et al.*:[1] a stoichiometric amount of 2-pyridinecarboxaldehyde was reacted with Mes*P(Li)$SiMe_2$(*t*-Bu) (**4**) at −65 °C in THF solution. After the reaction mixture was warmed to room temperature and worked up, *(E)*-**2** ($\delta(^{31}P) = 285$; $^2J(PH) = 25.4$ Hz) was isolated in 65% yield and 100% isomeric purity as air stable yellow crystals (Scheme 2); the conditions reported[1a] for the preparation of *(E)*-**2** were slightly adjusted, which led to higher yields, see Experimental Section. The ^1H NMR spectrum of *(E)*-**2** shows a characteristic signal of the *ortho*-proton of the pyridine ring at $\delta(^1H) = 8.5$; it proved to be important for monitoring η^1-coordination of the nitrogen atom to palladium *(vide infra)*. The phosphorus nucleus in *(E)*-**2** ($\delta(^{31}P) = 285$) is strongly deshielded compared to that in the phenyl analogue ($\delta(^{31}P) = 259$).[3b,c] This suggests a certain degree of conjugation between the electron withdrawing pyridine ring and the P=C double bond, whereby the π-electrons of the phosphaalkene are shifted toward the pyridine ring. Optimal conjugation requires a planar conformation of *(E)*-**2**; this was experimentally found in a crystal structure determination, which was reported to show the *s-trans* conformation exclusively.[1a]

We obtained yellow crystals of *(E)*-**2** (from acetonitrile), which were subjected to an X-ray crystal structure determination. The crystal contained *two* rotational conformers around the C(1)−C(8) bond in a disordered fashion; the *s-trans*:*s-cis* ratio was fixed at 1:1. The crystal structure of *(E)*-**2** has been reported earlier by Geoffroy *et al.*[1a] The magnitude and shape of the atomic displacement ellipsoids as well as the magnitude of the bond lengths strongly suggest that the pyridyl ring is also disordered in this earlier crystal structure determination, although no disorder model was introduced. The P(1)−C(1) (P=C) bond length is 1.663(3) Å, which is normal, and the C(1)−C(8) bond length is 1.470(4) Å, which is relatively short compared to the analogous bond length in other phosphaalkenes.[1d,3c,7a] The presence of two rotational conformers indicates that in the crystal, both conformations are practically equivalent which, in view of the minor differences between the *ortho*-pyridyl positions (C−H vs N), is not too surprising. The rotational barrier is expected to be so small that in solution, *(E)*-**2** will easily coordinate to a metal center in a bidentate *s-cis* fashion.

The structure of *(E)*-**2** (Figure 1, Table 1, 2) proves it to be almost planar, with dihedral angles of C(2)−P(1)−C(1)−C(8) = 178.5(2)° and P(1)−C(1)−C(8)−N(1) = −18(2)°. The C(1)−P(1)−C(2) angle is 99.15(14)°, which is small compared to the analogous angle in other phosphaalkenes.[7a] This implicates that the lone pair on phosphorus has relatively more s-character which is expected to result in weaker σ-bonding to transition metals.

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Table 1. Crystallographic Data for (*E*)-2 and 14

complex	(*E*)-**2**	**14**
	Crystal Data	
formula	$C_{24}H_{34}NP$	$C_{28}H_{45}NPPdSi$
mol wt	367.51	596.60
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	9.6550(6)	17.521(3)
b, Å	9.5829(5)	8.971(3)
c, Å	25.2514(14)	18.7463(19)
β, deg	112.108(5)	98.651(10)
V, Å^3	2164.6(2)	2913.0(11)
D_{calcd}, g cm^{-3}	1.128	1.360
Z	4	4
F(000)	800	1248
μ [Mo Kα], cm^{-1}	1.3	8.4
crystal size, mm	0.25 × 0.50 × 0.50	0.05 × 0.15 × 0.15
	Data Collection	
θ_{min}, θ_{max}, deg	1.7, 26.48	1.1, 27.5
$\Delta\omega$, deg	0.84 + 0.35 tan θ	0.50 + 0.35 tan θ
Hor., ver. aperture, mm	2.49 + 1.25 tan θ, 4.00	3.00 + 1.50 tan θ, 4.00
X-ray exposure time, h	9	39
linear instability, %	3	15
ref reflns	$0\bar{2}\bar{7}$,$4\bar{1}\bar{2}$,$\bar{2}\bar{2}2$	$\bar{2}2\bar{3}$,$\bar{2}2\bar{2}$,$\bar{2}3\bar{2}$
data set	−11:0, 0:12, −28:30	−22:22, −11:11, −24:16
total data	4509	17 502
total unique data	4246 [R_{int} = 0.039]	6677 [R_{int} = 0.081]
	Refinement	
no. of refined params	250	330
final R^a	0.0600 [3027 $F_o > 4\sigma(F_o)$]	0.0514 [4503 $F_o > 4\sigma(F_o)$]
final $wR2^b$	0.1444	0.1090
goodness of fit	1.06	1.01
weighting scheme^c	$[\sigma^2(F^2) + (0.0520P)^2 + 1.76P]^{-1}$	$[\sigma^2(F^2) + (0.0415P)^2 + 0.60P]^{-1}$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.000, 0.001	0.000, 0.002
min. and max. residual density, e Å^{-3}	−0.23, 0.33	−0.92, 0.65 [near Pd]

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

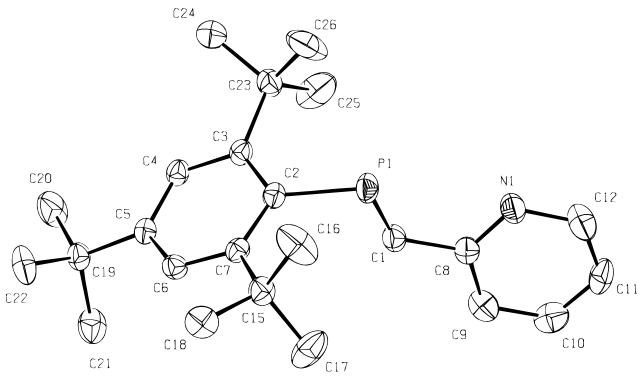


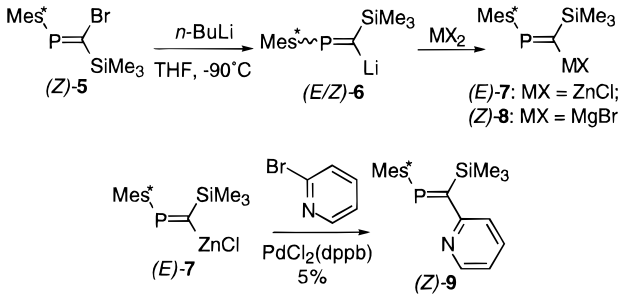
Figure 1. ORTEP[27] (30% probability level) drawing of (*E*)-**2**. Only one of the rotational conformers is shown; hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for (*E*)-2 (Esd in Parentheses)

	Bond Lengths		
P1−C1	1.663(3)	C10−C11	1.369(6)
C1−C8	1.470(4)	C11−C12	1.358(5)
C8−C9	1.33(5)	C12−N1	1.39(5)
C9−C10	1.38(5)	N1−C8	1.31(5)
	Bond Angles and Torsion Angles		
C1−P1−C2	99.15(14)	C11−C12−N1	120(2)
P1−C1−C8	123.8(2)	C12−N1−C8	119(4)
C1−C8−C9	118(2)	N1−C8−C1	119(2)
C8−C9−C10	119(4)	C2−P1−C1−C8	178.5(2)
C9−C10−C11	120(2)	P1−C1−C8−N1	−18(2)
C10−C11−C12	118.3(3)	C2−C3−C4−C5	2.5(4)

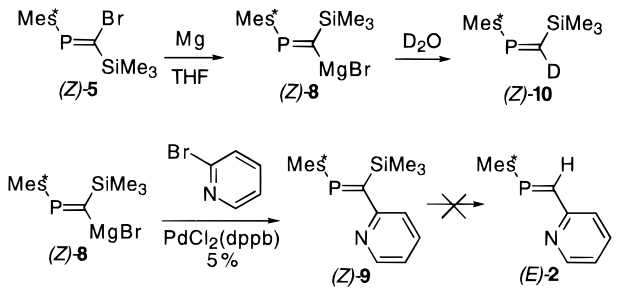
As in previous cases,[7a] the high degree of deshielding of the phosphorus nucleus cannot be explained by diamagnetic effects alone; presumably, paramagnetic effects associated with a lower HOMO−LUMO gap are also important.

Scheme 3



Although a stable pyridyl-functionalized phosphaalkene can be prepared by the classical route, we kept searching for the synthesis of such a species by a transition-metal-catalyzed cross-coupling reaction starting from halogen-substituted phosphaalkenes. Recently, we described investigations which led to reactive and configurationally stable 2-(trimethylsilyl)phosphaalkenylmetal halides Mes*P=C(SiMe$_3$)M (*(E)*-**7**, M = ZnCl; *(Z)*-**8**, M = MgBr) Scheme 3.[7b] These reagents were obtained by transmetalation of 2-lithio-2-(trimethylsilyl)phosphaalkenes *(E/Z)*-**6** with zinc dichloride or magnesium dibromide, respectively. The use of phosphaalkenylzinc chloride reagent *(E)*-**7** in transition-metal-catalyzed coupling reactions would be highly attractive from a synthetic point of view; it would facilitate the introduction of sensitive organic functionalities to the phosphaalkene moiety, such as carbonyl containing groups. We found an efficient method for the coupling of 2-bromopyridine with reagents *(E)*-**7** and

Scheme 4



(Z)-**8**. Minato *et al*. had described the analogous cross-coupling reaction between α-trimethylsilyl-substituted vinylmetallic reagents with 2-bromopyridines;[13] this coupling reaction was efficiently catalyzed by $PdCl_2$-(dppb) (dppb = 1,4-bis(diphenylphosphino)butane). When this catalyst (5 mol %) was applied in the cross-coupling reaction of *(E)*-**7** with 2-bromopyridine in refluxing THF solution for 6 h, the product *(Z)*-**9** ($\delta(^{31}P, CDCl_3) = 333$) was isolated in 56% yield (Scheme 3). The reaction was monitored by ^{31}P NMR spectroscopy of the crude reaction mixture. Besides the formation of *(Z)*-**9**, a substantial amount (35%) of the "protonated" product *(Z)*-Mes*P=C(H)SiMe$_3$ ($\delta(^{31}P$, crude reaction mixture) = 335; $J(PH) = 18$ Hz) was observed. The progress of the reaction was also monitored by hydrolysis of the zinc reagent *(E)*-**7**, as the phosphavinylidene reagents *(E)*-**7** and *(Z)*-**8** cannot be observed directly by ^{31}P NMR spectroscopy.[7b] The reaction was considered to be finished when the signal of the "hydrolysis product" ($\delta(^{31}P) = 335$) did not increase relative to that of *(Z)*-**9**, after adding water to a sample of the reaction mixture.

Extending these investigations, we discovered the first example of the direct formation of a Grignard reagent from the corresponding bromophosphaalkene. Previously, a methodology for the preparation of phosphaalkene Grignard reagents had not been reported, except for our transmetalation reaction of *(E/Z)*-**6** with magnesium dibromide, resulting in *(Z)*-**8**.7b Now, it turned out that Grignard reagent *(Z)*-**8** was formed by stirring a THF solution of *(Z)*-**5** with magnesium metal. Analysis of the reaction mixture by ^{31}P NMR spectroscopy after deuterolysis showed the mixture to contain only the deuterolysis product *(Z)*-**10** ($\delta(^{31}P$, crude reaction mixture) = 334) and the protonated product in a ratio of 87:13, corresponding to a 87% yield in Grignard reagent formation (Scheme 4). The remarkable inversion of configuration during this process is the subject of ongoing investigations, and the results will be reported in the near future.

The Grignard reagent *(Z)*-**8** was used for the palladium(II)-catalyzed coupling reaction with 2-bromopyridine. A mixture of *(Z)*-**8** and 2-bromopyridine was heated under reflux for 6 h in the presence of $PdCl_2$-(dppb) (5 mol %) in THF solution, as described above for the analogous zinc reagent *(E)*-**7**. After workup, 53% of the desired product *(Z)*-**9** was isolated (Scheme 4).

While we were able to prepare ligand *(E)*-**2** by the classical reaction *(vide supra)*, it was attractive to try the conversion of *(Z)*-**9** to *(E)*-**2** by exchanging the silyl group for a hydrogen atom (Scheme 4). The application of potassium fluoride in wet boiling DMF was described by Appel *et al*. in the analogous conversion of the phenyl derivative *(Z)*-Mes*P=C(SiMe$_3$)Ph.[12] However, their yield (approximately 50%) was disappointing and would not improve our methodology for the formation of *(E)*-**2**. We attempted to improve the conversion of *(Z)*-**9** by using other reagents. However, $KF \cdot 2H_2O$ in THF did not react and $Bu_4NF \cdot H_2O$ in THF gave decomposition products ($\delta(^{31}P) = 22$). Even lithium methoxide, which had been highly effective in the removal of a silyl group from the bromo analogue *(E)*-Mes*P=C(SiMe$_3$)Br,[7c] did not show any reactivity toward *(Z)*-**9**. These results clearly reveal that the formation of *(E)*-**2** from *(Z)*-**9** by a protio-desilylation reaction is not attractive from a synthetic point of view.

Formation and Reactivity of Palladium(II) Complexes. As described in the Introduction, the application of phosphaalkenes and phosphinines in bidentate ligands and their incorporation into new phosphaalkene- and phosphininemetal complexes attracts quite some interest, as these species may represent the phosphorus analogues of imine- and pyridinemetal complexes, which are widely explored for their use in homogeneous catalysis. Phosphaalkene-based ligands, such as *(E)*-**2** and *(Z)*-**9**, would be of interest for catalysis for several reasons. The electronic properties of the phosphaalkenes are different from those of imines. Calculations and photoelectron spectroscopic investigations have shown that in phosphaalkenes, the HOMO is usually of π-type, while the phosphorus lone pair σ-orbital is only slightly more stable.[14] In imines, however, the HOMO is the lone pair.[14] Additionally, the lone pair of a dicoordinate phosphorus atom has more s-character compared to that of comparable imines. Furthermore, the inherent polarity of the E=C double bond (E = P or N) is reversed due to the difference in the electronegativity (x) between the two heteroatoms: contrary to nitrogen ($x(N) = 3.0$), phosphorus ($x(P) = 2.1$) is slightly more electropositive compared to carbon ($x(C) = 2.5$).[16] These factors lead to weaker σ-coordination properties of the phosphorus lone pair compared to that of nitrogen. On the other hand, the phosphaalkene π^*-orbital (LUMO) is relatively low in energy and enhances the π^*-acceptor properties of these species in organometallic complexes, which would result in stronger back-bonding.[14] Moreover, ^{31}P NMR spectroscopy is a powerful tool for mechanistic studies on certain catalytic cycles in which the phosphaalkenes are involved.

Recently, Venanzi *et al*. reported on the formation and properties of transition metal (Pt(II), Ir(I)) complexes of 2-(2′-pyridyl)-4,5-dimethylphosphinine[15] and Geoffroy *et al*. reported the preparation of the 2-(2-pyridyl)-phosphaalkene complex [Cu(Mes*P=C(H)-(2-pyridyl))-(MeCN)$_2$][PF_6].[1a] We investigated the formation of palladium(II) complexes of *(E)*-**2** and *(Z)*-**9**. The palladium dichloride complexes **11** and **12** were obtained by reacting bis(benzonitrile)palladium dichloride with the bidentate ligands *(E)*-**2** and *(Z)*-**9**, respectively, in dichloromethane at room temperature for 10 min (Scheme 5). The complexes were isolated in 83% and

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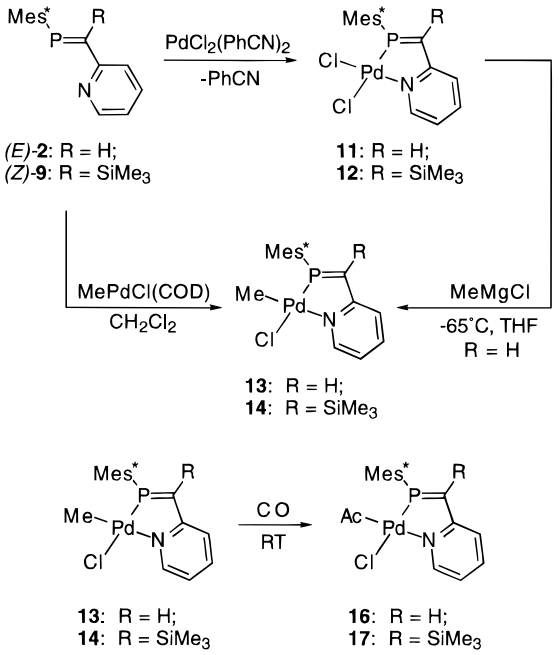
Scheme 5



91% yield, respectively, as yellow-orange powders. Complexation with palladium dichloride shows some characteristic features in the ^{1}H and ^{31}P NMR spectra of the ligands, which prove the presence of η^1,η^1-bonding of the ligands to the palladium(II) center. In the ^{1}H NMR spectra, a characteristic deshielding of the pyridine *ortho*-proton signal[8b] is observed; for **11** and **12** $\Delta\delta(^1\text{H}) = 1.36$ and 1.56, respectively. The phosphorus chemical shifts of the complexes show considerable shielding compared to the free ligands. For **11** ($\delta(^{31}\text{P}) = 247$) and **12** ($\delta(^{31}\text{P}) = 283$), a $\Delta\delta(^{31}\text{P})$ of -37.6 and -51.9 ppm is observed, respectively. This shielding is completely in line with the values reported in the case of other η1-phosphaalkene−palladium complexes.[1,3d]

Palladium complexes are of interest because of their potential application in catalysis, e.g., in carbon monoxide−olefin or carbon monoxide−acetylene copolymerization reactions. One of the important requirements for such a polymerization reaction is the possibility of a CO insertion reaction into a carbon−palladium bond of the corresponding complex. Complexes with a methyl−palladium bond can be used as models for investigating the ability of CO insertion.[8b,17]

For this reason, model complex **13** was prepared by reacting the palladium dichloride complex **11** with 1 equiv of methylmagnesium chloride in THF at −65 °C. The yellow suspension of **11** in THF changed into an orange solution immediately. At room temperature, the solvent was evaporated and the residue thoroughly washed with diethyl ether and pentane to furnish **13** as a yellow-orange powder (Scheme 5). In the ^{1}H NMR spectrum, a characteristic doublet of the methyl group at palladium ($\delta(^1\text{H}, \text{CDCl}_3) = 1.14$, d, $^3J(\text{HP}) = 3.99$ Hz) appeared. The ^{31}P NMR spectrum showed only one signal at $\delta(^{31}\text{P}) = 253$, proving the stereoselective substitution of only one chlorine atom. However, complex **13** was difficult to separate from the magnesium salts which are formed as byproducts. Therefore, an alternative procedure was used. Ligand *(E)*-**2** was reacted with 1 equiv of (1,5-cyclooctadiene)methylpalladium chloride[8] by stirring the reaction mixture in dichloromethane for 10 min at room temperature. After evaporation of the solvent and purification of the yellow product as described above, pure **13** was isolated as a yellow powder in 90% yield. Analogously, **14** ($\delta(^1\text{H}, \text{Pd}-\text{Me}, \text{CDCl}_3) = 1.11$, d, $^3J(\text{HP}) = 3.45$ Hz) was obtained from *(Z)*-**9** in 83% yield (Scheme 5).

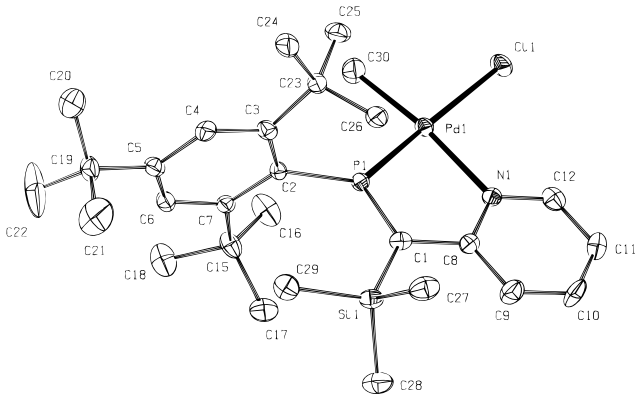


Figure 2. ORTEP[27] (30% probability level) drawing of **14**. Hydrogen atoms have been omitted for clarity.

In principle, the reactions leading to complexes **13** and **14** could furnish two stereoisomers; the methyl group might be positioned *trans* or *cis* toward the phosphorus center of the bidentate ligand. However, only one of the two possible products is formed with high selectivity. The methyl group is expected to be *cis* to the phosphorus center of the bidentate ligand because of its characteristic coupling value of $^3J(\text{HP}) = 3.99$ and 3.45 Hz, respectively, which is analogous to the $^3J(\text{HP})$ coupling constants of this magnitude in (PAN)MePdCl [PAN = 1-(dimethylamino)-8-(diphenylphosphino)naphthalene] complexes; according to the X-ray structure of this complex, the phosphorus atom and the methyl group are *cis* oriented.[18]

Structural Aspects of η^1,η^1-[Mes*P=C(SiMe$_3$)Py]-MePdCl (14). In order to unambiguously prove the structure of **14** and to obtain a better insight into the coordinative properties of ligand *(Z)*-**9** in **14**, we determined the X-ray crystal structure of this novel complex. The X-ray data were compared with those of [2-(*N*-(2-propyl)carbaldimino)-6-(methyl)pyridyl]methylpalladium(II) chloride ((*i*-Pr-6-Me−PyCa)MePdCl (**15**)),[8b] which can be considered as the imine analogue of **14** (Figure 2, Tables 1, 3, and 4).

Single crystals of **14** were obtained by slow concentration of a chloroform solution of the complex. The crystal structure shows a square planar arrangement of the ligands around the palladium center, and *(Z)*-**9** is indeed coordinated as a bidentate ligand to the MePdCl moiety. The methyl group bonded to palladium is positioned *cis* toward the coordinating phosphorus nucleus, in line with our expectation based on the small $^3J(\text{HP})$ value. The preference of the methyl group for the position *trans* toward the pyridine ring in **14** was also found in the case of **15**.[8b] This indicates that the phosphaalkene displays a stronger trans-influence[19] compared to the pyridine ligand. The C(1)−P(1)−C(2) angle is

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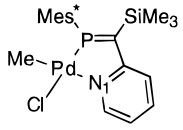
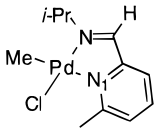
Table 3. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for 14 (Esd in Parentheses)

Bond Lengths			
P1−Pd1	2.1744(14)	C9−C10	1.371(8)
N1−Pd1	2.164(4)	C10−C11	1.370(7)
Pd1−C30	2.029(5)	C11−C12	1.380(7)
Pd1−C11	2.3545(14)	C12−N1	1.332(6)
C2−P1	1.808(4)	N1−C8	1.369(5)
C2−C3	1.431(5)	Si1−C1	1.911(4)
P1−C1	1.674(4)	Si1−C27	1.866(5)
C1−C8	1.478(5)	Si1−C28	1.866(6)
C8−C9	1.395(7)	Si1C29	1.856(5)
Bond Angles and Torsion Angles			
Pd1−P1−C1	110.98(15)	C11−C12−N1	123.7(4)
Pd1−N1−C8	119.3(3)	C12−N1−C8	119.2(4)
P1−Pd1−N1	79.45(10)	N1−C8−C1	118.2(3)
P1−Pd1−C30	95.40(15)	N1−Pd1−P1−C1	−0.2(2)
C30−Pd1−C11	88.75(15)	C2−P1−C1−C8	−174(4)
Cl1−Pd1−N1	96.85(10)	P1−C1−C8−N1	5.8(5)
C2−P1−C1	114.26(19)	P1−C1−Si1−C27	−121.6(3)
P1−C1−C8	111.8(3)	P1−C1−Si1−C28	118.9(3)
C1−C8−C9	122.9(4)	P1−C1−Si1−C29	−1.5(4)
C8−C9−C10	120.7(5)	C1−P1−Pd1−C30	174.6(2)
C9−C10−C11	119.8(5)	C8−N1−Pd1−Cl1	178.1(3)
C10−C11−C12	117.7(5)	C1−P1−C2−C3	86.3(3)

Table 4. Comparison of Bond Lengths (Å) and Bond Angles (deg) for 14 and 15[8b] (Esd in Parentheses)

		
	14	**15**
N-Pd		2.070(5)
P-Pd	2.1744(14)	
Pd-N(1)	2.164(4)	2.260(5)
Pd-Me	2.029(5)	2.009(9)
Pd-Cl	2.3545(14)	2.307(2)
Bite Angle	79.45(10)	78.4(2)

114.26(19)°, which is large compared to the analogous angle in [1,2-(diphosphaalkenyl)benzene]PdCl (111.3(5)°)[1d] but relatively small compared to that of (1,2-diphosphinidenecyclobutene)$PdCl_2$ (116.0(6)°)[3d] (Figure 2, Table 3).

Comparison of the bond lengths and bond angles of **14** with those of (*i*-Pr-6-Me-PyCa)MePdCl (**15**)[8b] is of interest (Table 4). The bonds of *(Z)*-**9** to the palladium nucleus are relatively strong. Compared to **15**, the Pd−N(1) bond is relatively short (Δd = −0.096(6) Å) and the Pd−Me and Pd−Cl bonds are relatively long (Δd = +0.019(10) and +0.048(2) Å, respectively). Comparison of the length of the P−Pd bond (d = 2.1744(14) Å) is not possible, as comparable complexes are not known. However, in the case of (1,2-diphosphinidenecyclobutene)-$PdCl_2$,[3d] longer P−Pd bond lengths of 2.235(4) and 2.242(4) Å were found, which is probably due to the larger bite angle of this ligand. The bite angle (P−Pd−N(1)) of *(Z)*-**9** in **14** is 79.45(10)°, which is only slightly larger (Δ = +1.0(2)°) than that of **15** (N−Pd−N(1); 78.4(2)°, Table 4).[8b]

Although the discussion of the trans-influence exclusively in terms of π-back-bonding is controversial,[19] it does explain our observations. The longer Pd−Cl bond in **14** compared to that of **15** (Table 4) suggests a stronger trans-influence, or back-bonding, of the phosphaalkene compared to the imine moiety, which must have its origin in an energetically lower π*-orbital. Indeed, the calculated lower energy of the π*-orbital (LUMO) of a phosphaalkene compared to that of an imine is capable of increasing the back-donation of the metal dπ-orbital to the phosphaalkene pπ*-orbital.[14] As a consequence, the P(1)−Pd bond is expected to be relatively short and strong, as experimentally observed (*vide supra*).

It should be noted that the Pd−N(1) bond is also shorter than the corresponding bond in **15**. For **14**, this might imply a stronger back-bonding to the pyridine ring, too. As a result, the Pd−Me bond is lengthened. Analogous simultaneous shortening of ligand−palladium bonds was also observed when two (*i*-Pr-6-R−PyCa)-MePdCl (R = Me, C(O)H) complexes were compared.[8b]

CO Insertion Reactions. The relative extent of back-bonding from the palladium center to the pyridine ring should influence the C=O stretching frequencies of the acetyl derivatives derived from **13**, **14**, and **15** by CO insertion. Stronger back-bonding from palladium to the pyridine moiety must decrease the amount of back-bonding to the *trans*-acetyl C=O π*-orbital, resulting in a stronger C=O double bond and, therefore, higher infrared absorption frequencies.

In order to verify these assumptions, we performed preliminary experiments to test the activity of **13** and **14** toward CO insertion by bubbling CO under atmospheric pressure through a deuterochloroform solution of the complex in a NMR tube at room temperature. The progress of the reaction was monitored by ^{31}P NMR spectroscopy, showing the appearence of a new signal at $\delta(^{31}P)$ = 244 and $\delta(^{31}P)$ = 292, respectively. The ^1H NMR spectrum showed a characteristic downfield shift of the methyl−palladium signal to the region of acetyl−palladium compounds,[8b,17,18] indicating the formation of the CO insertion products **16** and **17** (Scheme 5). For **16** and **17**, a singlet was found at $\delta(^1H, CDCl_3)$ = 2.56 and 2.54, respectively. Although formation of some palladium black was observed during the formation of these acetyl complexes, the complexes were stable at room temperature: a solution of **16** or **17** stored in $CDCl_3$ in the NMR tube for 1 week showed no change in the ^1H NMR spectra.

The rate of the CO insertion reaction was not measured quantitatively, but the formation of **16** was finished within 1 h, while the formation of **17** was slower; only 10% conversion was observed after 2 h. These conversions are relatively slow compared to those of the comparable (R−PyCa)MePdCl complexes. The latter usually show 50% conversion to the acetyl derivatives within 4−30 min.[8b]

The insertion of carbon monoxide was confirmed by IR spectroscopy (KBr pellets). The insertion of CO in **13** and **14** led to the appearence of a carbonyl absorption at ν(CO) = 1711 and 1701 cm^{-1} for complexes **16** and **17**, respectively. These values are relatively large compared to those for (*i*-Pr-6-R−PyCa)AcPdCl (**18**, ν(CO) = 1692−1697 cm^{-1}) and (bipy)AcPdCl (**19**, ν(CO) = 1690 cm^{-1}).[8b]

In the series **19**, **18**, **16**, and **17**, changing the *ortho*-substituent at pyridine increases the C=O stretching

(19) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

frequency in the order pyridine < imine < phosphaalkene. The frequencies of **16** and **17** fall in the range of those for normal carbonyl compounds (aldehydes, ν(CO) = 1725−1705 cm^{-1}). The lower absorption frequency of **19** falls in the characteristic absorption range of the strongly conjugated amides (ν(CO) = 1650−1690 cm^{-1}). These observations agree with an increase in palladium to *trans*-pyridine back-bonding in the order: **19** < **18** < **17** < **16**. Thus, a direct correlation between the degree of back-bonding of palladium to the pyridine moiety and the CO stretching frequency of the *trans*-acetyl group seems indicated.

Although the increase of Pddπ−N(Py)pπ* back-bonding might not be the only explanation for the observed correlation, the correlation between the LUMO energy of the pyridine, imine, and phosphaalkene moiety and the CO stretching frequency of the adjacent acetyl group still holds. Perhaps the observed trend is better described by the controversial "*cis*-influence"[19] of the pyridine, imine, and phosphaalkene moiety: stronger back-bonding to this ligand results in weaker back-bonding of palladium to the *cis*-acetyl group, leading to stronger C═O bonds. Nevertheless, a more detailed theoretical analysis will be necessary to fully understand the factors involved.

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 and Bruker MSL 400 spectrometer (^{1}H, ^{13}C) or with a Bruker WM 250 spectrometer (^{31}P). Tetramethylsilane (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P) was used as an external standard. 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. Infrared spectra were measured by using KBr pellets with a Matteson Galaxy 6030 FTIR. Elemental analyses were performed by Microanalytisches Labor Pascher, Remagen, Germany. Compounds *(E)*-**1**,[7c] *(Z)*-**5**,[7b,c] *(E)*-**7**,[7b] 2-pyridylmagnesium bromide,[10] 2-(trimethylstannyl)pyridine,[11] and MePdCl(COD)[8a] were prepared according to literature procedures.

***(E)*-((2-Pyridyl)methylene)(2,4,6-tri-*tert*-butylphenyl)-phosphine (2).** This compound was prepared according to the procedure of Geoffroy *et al.*,[1a] but with a slight adjustment: performing the Peterson olefination at −65 °C and addition of trimethylsilyl chloride at room temperature resulted in higher yields and one stereoisomer only. A solution of *n*-butyllithium in hexane (5.86 mL, 1.6 M, 9.36 mmol) was added to a solution of Mes*PH_2 (2.61 g, 9.36 mmol) in THF (100 mL) at −65 °C, furnishing a yellow/orange precipitate. Afterward, the reaction mixture was warmed to room temperature, furnishing a dark red solution. After the solution was stirred for 15 min at ambient temperature, dimethyl(*tert*-butyl)silyl chloride (1.41 g, 9.36 mmol) was added all at once. After the solution was stirred again for 15 min, *n*-butyllithium in hexane (5.86 mL, 1.6 M, 9.36 mmol) was added to the solution at room temperature. After 15 min of stirring at room temperature, the reaction mixture was cooled to −65 °C and 2-pyridinecarboxaldehyde (1.00 g, 9.36 mmol) was added. After the reaction mixture was warmed to room temperature, trimethylsilyl chloride (1.02 g, 9.36 mmol) was added, furnishing a yellow/orange solution. The solvent was evaporated, the residue was extracted with pentane, and the extract was filtered. After evaporation of the pentane from the filtrate, the residue was crystallized from acetonitrile, funishing yellow crystals (yield: 2.24 g, 6.08 mmol, 65%); mp 132−134 °C (lit.:[1a] 142−144 °C). ^{1}H NMR ($CDCl_3$): δ 1.27 (s, 9H, *p*-*t*-Bu), 1.44 (s, 18H, *o*-*t*-Bu), 7.00 (m, 1H, Py*H*), 7.25 (m, 1H, Py*H*), 7.36 (d, 2H, ^4J(HP) = 1.2 Hz, Ar*H*), 7.48 (m, 1H, Py*H*), 8.01 (d, 1H, ^2J(HP) = 25.4 Hz, P═C*H*), 8.50 (d, 1H, *J*(HH) = 3.9 Hz, Py*H*). ^{13}C{^{1}H}NMR ($CDCl_3$): δ 31.3 (s, *p*-C(CH_3)$_3$), 33.8 (d, ^4J(CP) = 7.2 Hz, *o*-C(CH_3)$_3$), 34.8 (s, *p*-*C*(CH_3)$_3$), 38.1 (s, *o*-*C*(CH_3)$_3$), 120.9 (d, *J*(CP) = 17.7 Hz, Py), 121.7 (s, *m*-Ar), 121.9 (d, *J*(CP) = 6.9 Hz, Py), 136.4 (d, *J*(CP) = 2.31 Hz, Py), 138.8 (d, ^1J(CP) = 53.9 Hz, *ipso*-Ar), 149.8 (d, ^2J(CP) = 4.8 Hz, *o*-Ar), 153.9 (s, *p*-Ar), 157.8 (d, *J*(CP) = 13.5 Hz, Py), 173.9 (d, ^1J(CP) = 34.0 Hz, P═*C*). ^{31}P NMR ($CDCl_3$): δ 285. MS (70 eV): *m*/*z* (1, M^+), 310 (100, M^+ − *t*-Bu). HRMS: calcd. for $C_{24}H_{34}PN$, 367.2429; found, 367.2428. Anal. Calcd for $C_{24}H_{34}PN$: C, 78.43; H, 9.33; P, 8.43. Found: C, 78.15; H, 9.47; P, 8.28.

***(E)*-(Trimethylstannylmethylene)(2,4,6-tri-*tert*-butylphenyl)phosphine (3).** At room temperature, THF (5 mL) was added to a mixture of *(E)*-**1** (0.18 g, 0.5 mmol), chlorotrimethylstannane (0.12 g, 0.6 mmol), and magnesium (0.024 g, 1.00 mmol). The reaction mixture was stirred for 1 h. The solvent was evaporated, and the residue was extracted with pentane. Evaporation of the pentane furnished *(E)*-**3** as a yellowish oil, which was used without further purification (yield: 0.19 g, 0.44 mmol, 87%). ^{1}H NMR ($CDCl_3$): δ 0.29 (s, 9H, $SnMe_3$), 1.38 (s, 9H, *p*-*t*-Bu), 1.56 (s, 18H, *o*-*t*-Bu), 7.42 (s, 2H, Ar*H*), 8.32 (d, 1H, ^2J(HP) = 26.2 Hz, P═C*H*). ^{31}P NMR ($CDCl_3$): δ 323. Spectra were identical with those reported.[20]

***(Z)*-((2-Pyridyl)(trimethylsilyl)methylene)(2,4,6-tri-*tert*-butylphenyl)phosphine (9).** From (*E*)-**7**: At room temperature, a solution of *(E)*-**7** (4 mmol) in THF (10 mL) was added to a suspension of 2-bromopyridine (0.63 g, 4 mmol), bis(benzonitrile)palladium dichloride (0.076 g, 0.20 mmol), and 1,4-bis(diphenylphosphino)butane (0.085 g, 0.20 mmol) in THF (5 mL). The suspension was heated under reflux for 6 h, furnishing an orange solution. The solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane. Silica was added, and the dichloromethane was evaporated. The residue was added on top of a small silica column. The column was flushed with dichloromethane. Evaporation of the dichloromethane and crystallization of the residue from hot acetonitrile furnished yellowish crystals (yield: 0.98 g, 2.24 mmol, 56%). The spectral data were identical with those of **9** prepared as described below.

From (*Z*)-**8**: Compound *(Z)*-**5** (0.88 g, 2 mmol) was mixed with sublimed magnesium (0.096 g, 4 mmol) and dibromoethane (0.05 mL, 0.11 g, 0.59 mmol). The exothermic reaction was started by the slow addition of THF (20 mL). The orange solution was stirred overnight and was added to a THF (10 mL) solution of 2-bromopyridine (0.32 g, 2.0 mmol), bis(benzonitrile)palladium dichloride (5 mol %, 0.038 g, 0.100 mmol), and 1,4-bis(diphenylphosphino)butane (0.043 g, 0.100 mmol). The mixture was heated under reflux for 6 h. The product was isolated as described above furnishing **9** (yield: 0.48 g, 1.1 mmol, 53%); mp 160−161 °C. ^{1}H NMR ($CDCl_3$): δ −0.30 (s, 9H, $SiMe_3$), 1.39 (s, 9H, *p*-*t*-Bu), 1.64 (s, 18H, *o*-*t*-Bu), 7.17 (m, 1H, Py*H*), 7.44 (m, 1H, Py*H*), 7.45 (s, 2H, Ar*H*), 7.70 (m, 1H, Py*H*), 8.55 (d, 1H, *J*(HH) = 3.8 Hz, Py*H*). ^{13}C{^{1}H}NMR ($CDCl_3$): δ −0.9 (s, Si(*C*H_3)$_3$), 31.2 (s, *p*-C(*C*H_3)$_3$), 33.5 (d, ^4J(CP) = 7.7 Hz, *o*-C(*C*H_3)$_3$), 34.9 (s, *p*-*C*(*C*H_3)$_3$), 38.2 (s, *o*-*C*(CH_3)$_3$), 120.5 (s, Py), 121.7 (s, *m*-Ar), 121.9 (s, Py), 135.7 (s, Py), 138.5 (d, ^1J(CP) = 56.6 Hz, *ipso*-Ar), 148.6 (s, *o*-Ar), 150.5 (s, *p*-Ar), 153.9 (s, Py), 165.5 (d, ^1J(CP) = 31.5 Hz, P═*C*). ^{31}P NMR ($CDCl_3$): δ 333. MS (70 eV): *m*/*z* (1, M^+), 382 (100, M^+ − *t*-Bu). HRMS: Calcd for $C_{27}H_{42}PN^{28}Si$, 439.2824; found, 439.2818. Anal. Calcd for $C_{27}H_{42}PNSi$: C, 73.75; H, 9.63; N, 3.18. Found: C, 71.79; H, 9.76; N, 3.08.

***η*^{1},*η*^{1}-[*(E)*-((2-Pyridyl)methylene)(2,4,6-tri-*tert*-butylphenyl)phosphine]palladium Dichloride (11).** A mixture of *(E)*-**2** (0.37 g, 1.00 mmol) and bis(benzonitrile)palladium dichloride (0.37 g, 1.00 mmol) was dissolved in dichlo-

(20) Goede, S. J.; Bickelhaupt, F. *Chem. Ber.* **1991**, *124*, 2677.

romethane (4 mL) at room temperature. The mixture was stirred for 15 min at ambient temperature. The product was precipitated by adding pentane (40 mL). The solvent was removed and the residue dried *in vacuo* furnishing a microcrystalline orange solid, which was crystallized from chloroform furnishing orange needles (yield: 0.45 g, 0.83 mmol, 83%); mp 175−180 °C (dec). ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 9H, *p*-*t*-Bu), 1.70 (d, 18H, ^5J(HP) = 1.75 Hz, *o*-*t*-Bu), 7.34 (m, 1H, Py*H*), 7.35 (d, 1H, ^2J(HP) = 22.7 Hz, P=C*H*), 7.56 (d, 2H, ^4J(HP) = 7.56 Hz, Ar*H*), 7.62 (m, 1H, Py*H*), 7.85 (m, 1H, Py*H*), 9.86 (d, 1H, J(HH) = 5.9 Hz, Py*H*). ^{13}C{^{1}H}NMR ($CDCl_3$): δ 30.9 (s, *p*-C(CH_3)$_3$), 35.0 (s, *o*-C(CH_3)$_3$), 35.4 (d, ^5J(CP) = 1.0 Hz, *p*-*C*(CH_3)$_3$), 39.3 (d, ^3J(CP) = 1.8 Hz, *o*-*C*(CH_3)$_3$), 117.5 (d, ^1J(CP) = 17.6 Hz, *ipso*-Ar), 122.8 (d, J(CP) = 38.5 Hz, Py), 122.9 (s, Py), 124.0 (d, ^3J(CP) = 10.7 Hz, *m*-Ar), 140.2 (d, J(CP) = 4.1 Hz, Py), 150.5 (d, ^1J(CP) = 54.3 Hz, P=*C*), 154.4 (d, J(CP) = 5.2 Hz, Py), 156.0 (d, ^4J(CP) = 3.3 Hz, *p*-Ar), 157.3 (d, ^2J(CP) = 3.3 Hz, *o*-Ar), 159.1 (d, J(CP) = 6.7 Hz, Py). ^{31}P NMR ($CDCl_3$): δ 247. Anal. Calcd for $C_{24}H_{34}PNPdCl_2$: C, 52.91; H, 6.29; Pd, 19.5. Found: C, 49.90; H, 6.08; Pd, 19.5.

***η*^{1},*η*^{1}-[*(Z)*-((2-Pyridyl)(trimethylsilyl)methylene)(2,4,6-tri-*tert*-butylphenyl)phosphine]palladium Dichloride (12).** A mixture of **9** (0.44 g, 1.00 mmol) and bis(benzonitrile)-palladium dichloride (0.37 g, 1.00 mmol) was dissolved in dichloromethane (4 mL) at room temperature. The mixture was stirred for 15 min at ambient temperature. The product was precipitated from the solution by adding pentane (40 mL). The solvent was removed and the residue dried *in vacuo* furnishing a microcrystalline yellow solid (yield: 0.56 g, 0.91 mmol, 91%); mp 230−231 °C. ^{1}H NMR ($CDCl_3$): δ −0.00 (s, 9H, $SiMe_3$), 1.37 (s, 9H, *p*-*t*-Bu), 1.77 (d, ^5J(HP) = 1.6 Hz, 18H, *o*-*t*-Bu), 7.3 (m, 1H, Py*H*), 7.61 (d, ^4J(HP) = 4.5 Hz, 2H, Ar*H*), 7.9 (m, 1H, Py*H*), 10.11 (d, ^1J(HH) = 6.0 Hz, 1H, Py*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.55 (d, ^4J(HP) = 1.4 Hz, Si(*C*H)$_3$), 30.8 (s, *p*-C(*C*H_3)$_3$), 35.6 (s, *o*-C(*C*H_3)$_3$), 35.9 (d, *p*-*C*(CH_3)$_3$), 40.0 (d, ^3J(CP) = 1.5 Hz, *o*-*C*(CH_3)$_3$), 118.8 (d, ^1J(CP) = 20.0 Hz, *ipso*-Ar), 122.8 (d, J(CP) = 8.1 Hz, Py), 123.4 (d, J(CP) = 31.4 Hz, Py), 125.0 (d, ^3J(CP) = 10.6 Hz, *m*-Ar), 139.6 (d, J(CP) = 3.2 Hz, Py), 155.2 (d, J(CP) = 4.2 Hz, Py), 156.0 (d, ^4J(CP) = 3.1 Hz, *p*-Ar), 156.2 (d, ^2J(CP) = 3.4 Hz, *o*-Ar), 160.9 (d, ^1J(CP) = 26.0 Hz, P=*C*), 163.2 (d, J(CP) = 3.6 Hz, Py). ^{31}P NMR ($CDCl_3$): δ 283. Anal. Calcd for $C_{27}H_{42}Cl_2PPdNSi$: C, 52.56; H, 6.87; N, 2.27; Pd, 17.24. Found: C, 51.22; H, 6.83; N, 2.65; Pd, 18.1.

***η*^{1},*η*^{1}-[*(E)*-((2-Pyridyl)methylene)(2,4,6-tri-*tert*-butylphenyl)phosphine]methylpalladium Chloride (13).** From **11**: At −65 °C, a solution of methylmagnesium chloride (3 M, 0.5 mL, 1.5 mmol) was added to a yellow suspension of **11** (0.82 g, 1.5 mmol) in THF (15 mL). An orange solution was formed immediately. After the mixture was warmed to room temperature, the solvent was evaporated and the solid residue was washed thoroughly with ether (20 mL), resulting in an orange/yellow powder, which was contaminated with magnesium salts (yield: 0.63 g). The spectral data were identical with those of **13** prepared as described below.

From **2** and MePdCl(COD): Dichloromethane (5 mL) was added to a mixture of **2** (0.18 g, 0.5 mmol) and MePdCl(COD) (0.13 g, 0.5 mmol) at room temperature. The orange/yellow solution was stirred for 10 min. The solvent was evaporated under reduced pressure, and the yellow solid residue was washed twice with a mixture of ether and pentane (50/50, 5 mL). Drying the solid *in vacuo* furnished a yellow powder (yield: 0.24 g, 0.45 mmol, 90%); mp 195−197 °C (dec). ^{1}H NMR ($CDCl_3$): δ 1.14 (d, 3H, ^3J(HP) = 3.99 Hz, Me−Pd) 1.33 (s, 9H, *p*-*t*-Bu), 1.60 (s, 18H, *o*-*t*-Bu), 7.15 (m, 1H, Py*H*), 7.31 (m, 1H, Py*H*), 7.54 (d, 2H, ^4J(HP) = 3.44 Hz, Ar*H*), 7.67 (m, 1H, Py*H*), 7.69 (d, 1H, ^2J(HP) = 21.7 Hz, P=C*H*), 9.37 (d, 1H, J(HH) = 5.09 Hz, Py*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ −0.5 (d, ^2J(CP) = 2.6 Hz, Me−Pd), 31.0 (s, *p*-C(*C*H_3)$_3$), 34.1 (d, ^4J(CP) = 1.7 Hz, *o*-C(*C*H_3)$_3$), 35.4 (d, *p*-*C*(CH_3)$_3$), 39.0 (d, ^3J(CP) = 1.4 Hz, *o*-*C*(CH_3)$_3$), 121.0 (d, J(CP) = 24.1 Hz, Py), 121.9 (d, ^1J(CP) = 6.7 Hz, *ipso*-Ar), 123.1 (d, ^3J(CP) = 8.6 Hz, *m*-Ar), 138.7 (d, J(CP) = 3.3 Hz, Py), 151.2 (d, J(CP) = 4.1 Hz, Py), 154.2 (d, ^4J(CP) = 2.7 Hz, *p*-Ar), 155.8 (d, ^1J(CP) = 51.7 Hz, P=*C*), 156.7 (d, ^2J(CP) = 2.3 Hz, *o*-Ar), 157.2 (d, J(CP) = 4.0 Hz, Py). ^{31}P NMR ($CDCl_3$): δ 253. Anal. Calcd for $C_{25}H_{37}ClNPPd$: C, 57.26; H, 7.12; Cl, 6.76; Pd, 20.29. Found: C, 57.51; H, 7.06; Cl, 6.83; Pd, 19.9.

***η*^{1},*η*^{1}-[*(Z)*-((2-Pyridyl)(trimethylsilyl)methylene)(2,4,6-tri-*tert*-butylphenyl)phosphine]methylpalladium Chloride (14).** Dichloromethane (5 mL) was added to a mixture of **9** (0.21 g, 0.5 mmol) and MePdCl(COD) (0.13 g, 0.5 mmol) at room temperature. The orange/yellow solution was stirred for 10 min. The solvent was evaporated under reduced pressure, and the yellow solid residue was washed twice with pentane (5 mL). The solid was dried *in vacuo* furnishing a yellow-orange, powder which was crystallized from ether (yield: 0.25 g, 0.42 mmol, 83%); mp 195−198 °C (dec). ^{1}H NMR ($CDCl_3$): δ 0.00 (s, 9H, $SiMe_3$), 1.11 (d, 3H, ^3J(HP) = 3.45 Hz, Me−Pd), 1.40 (s, 9H, *p*-*t*-Bu), 1.70 (s, 18H, *o*-*t*-Bu), 7.44 (m, 1H, Py*H*), 7.56 (m, 1H, Py*H*), 7.64 (d, 2H, ^4J(HP) = 3.56 Hz, Ar*H*), 7.84 (m, 1H, Py*H*), 9.62 (m, 1H, Py*H*). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 0.1 (d, ^3J(CP) = 3.0 Hz, $SiMe_3$), 3.2 (d, ^2J(CP) = 4.6 Hz, Me−Pd), 31.0 (s, *p*-C(*C*H_3)$_3$), 34.9 (s, *o*-C-(*C*H_3)$_3$), 35.3 (s, *p*-*C*(CH_3)$_3$), 39.8 (d, *o*-*C*(CH_3)$_3$), 122.2 (d, J(CP) = 25.1 Hz, Py), 122.7 (d, J(CP) = 7.3 Hz, Py), 122.9 (d, ^1J(CP) = 7.1 Hz, *ipso*-Ar), 124.9 (d, ^3J(CP) = 8.7 Hz, *m*-Ar), 138.1 (d, J(CP) = 1.9 Hz, Py), 151.6 (d, J(CP) = 2.3 Hz, Py), 154.6 (d, ^4J(CP) = 2.5 Hz, *p*-Ar), 155.6 (d, ^2J(CP) = 2.6 Hz, *o*-Ar), 160.7 (d, J(CP) = 3.4 Hz, Py), 163.8 (d, ^1J(CP) = 25.0 Hz, P=*C*). ^{31}P NMR ($CDCl_3$): δ 295. Anal. Calcd for $C_{28}H_{45}ClNPPdSi$: C, 56.37; H, 7.61; Cl, 5.94; Pd, 17.8. Found: C, 56.37; H, 7.60; Cl, 6.27; Pd, 17.4.

General Procedure for the Preparation of 16 and 17. Through a NMR tube containing complex **13** or **14** in $CDCl_3$, respectively, was bubbled carbon monoxide gas at room temperature under atmospheric pressure, during which time the color changed from yellow to orange/red. The formation of **16** was complete within 1 h. The formation of **17** had proceeded only halfway after approximately 1 day of reaction. The insertion of CO was monitored by ^{31}P and ^{1}H NMR spectroscopies and by IR spectroscopy.

***η*^{1},*η*^{1}-[*(E)*-((2-Pyridyl)methylene)(2,4,6-tri-*tert*-butylphenyl)phosphine]acetylpalladium Chloride (16).** ^{1}H NMR ($CDCl_3$): δ 1.28 (s, 9H, *p*-*t*-Bu), 1.59 (s, 18H, *o*-*t*-Bu), 2.56 (s, 3H, Ac−Pd) 7.05 (m, 1H, Py*H*), 7.26 (m, 1H, Py*H*), 7.47 (d, 2H, ^4J(HP) = 3.19 Hz, Ar*H*), 7.63 (m, 1H, Py*H*), 7.63 (d, 1H, ^2J(HP) = 23.8 Hz, P=C*H*), 9.25 (d, 1H, J(HH) = 4.28 Hz, Py*H*). ^{31}P NMR ($CDCl_3$): δ 244. IR (KBr): ν(CO) 1711 cm^{-1}.

***η*^{1},*η*^{1}-[*(Z)*-((2-Pyridyl)(trimethylsilyl)methylene)(2,4,6-tri-*tert*-butylphenyl)phosphine]acetylpalladium Chloride (17).** ^{1}H NMR ($CDCl_3$): δ 0.09 (s, 9H, $SiMe_3$), 1.32 (s, 9H, *p*-*t*-Bu), 1.68 (d, 18H, ^5J(HP) = 1.25 Hz, *o*-*t*-Bu), 2.54 (s, 3H, Ac−Pd) 7.39 (m, 1H, Py*H*), 7.51 (d, 2H, Ar*H*), 7.56 (m, 1H, Py*H*), 7.75 (m, 1H, Py*H*), 9.38 (d, 1H, J(HH) = 5.41 Hz, Py*H*). ^{31}P NMR ($CDCl_3$): δ 292. IR (KBr): ν(CO) 1701 cm^{-1}.

X-ray Structure Determination of *(E)*-2 and 14. Crystals of *(E)*-**2** (yellow) and **14** (orange) suitable for X-ray diffraction were glued to the tip of a Lindemann-glass capillary and transferred into the cold nitrogen stream of 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[21]), in the range 10.34° < θ < 13.93° and 11.69° < θ < 13.92° for *(E)*-**2** and **14**, respectively. Reduced-cell calculations did not indicate higher lattice symmetry.[22] Crystal data and details on data collection and refinement are given in Table 1. Data were collected at 150 K in ω scan mode using graphite-monochromated Mo Kα

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radiation ($\lambda = 0.710\ 73$ Å). Data were corrected for *Lp* effects and for the observed linear instability of the reference reflections, but not for absorption. The structure of *(E)*-**2** was solved by automated direct methods (SHELXs 86[23]). The structure of **14** was solved by automated Patterson methods and subsequent differnce Fourier techniques (DIRDIF-92[24]). Both compounds were refined on $F^{2\prime\prime}$ by full-matrix least-squares techniques (SHELXL-93[25]); no observance criterion was applied during refinement. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The methyl groups of both compounds were refined as rigid groups, allowing for rotation around the C−C, Pd−C, or Si−C bonds. The pyridine ring of *(E)*-**2** was included in the refinement in two positions, related by a 180° rotation over C(1)−C(8). Although all positional parameters of *(E)*-**2** were freely refined, the anisotropic displacement parameters of the N,C couples located at approximately the same position were equated. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms by a factor amounting to 1.5 for the methyl hydrogen atoms and 1.2 for the other hydrogen atoms. Neutral-atom scattering factors and anomalous dispersion corrections were taken from the *International Tables for Crystallography*.[26] Geometrical calculations and illustrations were performed with PLATON;[27] all calculations were performed on a DECstation 5000 cluster.

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Supporting Information Available: Tables of further details of the structure determination, including atomic coordinates, bond lengths and angles, and thermal parameters for *(E)*-**2** and **14** (14 pages). Ordering information is given on any current masthead page.

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