Chemistry of P,N-Ligated Methylpalladium(II) Alkoxide Complexes: Syntheses, Structural Features in the Solid State and in Solution, and Hydrogen-Bond Formation

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The reaction of P,N-ligated dimethylpalladium(II) complexes [$Pd(Me)_2(P{\sim}N)$] [P∼N = *o*-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine (PCN), (diphenylphosphino)-*N*,*N*-dimethylethyleneamine (PN)] with an equimolar amount of $HOCH(CF_3)_2$ or HOC_6H_4-4-X (X = H, Cl, OMe, Me, CN, NO_2, OH) affords methylpalladium(II) alkoxide and aryl oxide complexes [$Pd(Me)(OR)(P{\sim}N)$] [R = $CH(CF_3)_2$, C_6H_4-4-X; P∼N = PCN, PN], which have been isolated in high yields as white or pale orange solids. NMR spectroscopic data indicate that the complexes have the alkoxide or aryl oxide ligand (OR) positioned trans with respect to the P-atom. Reaction of [$Pd(Me)_2$(PCN)] with 2 equiv of phenol affords the phenol adduct [$Pd(Me)(OC_6H_5)$(PCN)]·HOC_6H_5, which has been isolated as a white solid. The transesterification reaction of [$Pd(Me)(OC_6H_5)$(PCN)] with $C_6H_5SC(O)Me$ affords the arenethiolate complex [$Pd(Me)(SC_6H_5)$(PCN)]. Furthermore, the alkoxide complex [$Pd(Me)(OCH(CF_3)_2)$(PN)] reacts with phenylacetylene to afford an isolable alkynylpalladium(II) complex [Pd(Me)(C≡CPh)(PN)]. Thermolysis of the latter complex results in reductive elimination of MeC≡CPh in 98% yield. When this reductive elimination is performed under a CO atmosphere, MeC≡CPh (87%) is formed together with small amounts of the insertion product, MeC(O)C≡CPh (3%). Crystals of [$Pd(Me)(OC_6H_5)$(PCN)]·CH_2Cl_2 and its adduct with HOC_6H_5 have been subjected to X-ray diffraction studies. The molecular structure of the latter adduct shows an O−H···O hydrogen bond between the phenol and the oxygen atom of the phenoxide unit. The ^{31}P NMR chemical shift and $^3J_{H,P}$ for the Pd−CH_3 group of the complexes [$Pd(Me)(OC_6H_4$-4-X)(PN)] have been correlated with various Hammet substituent constants; the best linearity was achieved with parameters that represent the sum of resonance and inductive/field effects of the substituent X.

Introduction

One reason for the recent interest in the chemistry of late transition metal alkoxides is that such complexes have been postulated as intermediates in various metal complex-catalyzed synthetic organic reactions.[1] Examples of alkoxypalladium-catalyzed processes include not only the copolymerization of CO and olefins to produce polyketones[2] but also the methoxycarbonylation of propyne to give methyl methacrylate.[3] Research in late transition metal alkoxide chemistry may have been limited by the earlier belief that the transition metal-to-oxygen bond is weak, particularly when the other ligands are mono- or bidentate tertiary amines.[4] However, it is now recognized that the metal-to-oxygen bond can be of comparable strength or even stronger than the metal-to-carbon(sp^3) bond.[5]

Reported interesting properties of late transition metal alkoxides include C−O bond formation,[6] insertion of small molecules into the metal-to-oxygen bond,[7] *β*-hydrogen elimination of the alkoxide ligand to release aldehydes or ketones,[8] and their ability to associate with alcohols through O−H···O hydrogen bonding.[9] In the course of our study concerning palladium alkoxides,[10] we have reported both the synthesis and properties of methylpalladium(II) alkoxides (and their adducts with

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alcohols) containing bidentate N-donor ligands,[11] as well as the reaction of CO with N-ligated methylpalladium methoxides that affords stable methylpalladium methoxycarbonyl complexes.[12] These studies and the use of P,N-ligating ligands in the palladium methoxide-catalyzed production of methyl methacrylate[3] encouraged us to use bidentate P,N-donor ligands in palladium alkoxide chemistry. Here, we report full details of our study on the synthesis, properties, and reactivity of P,N-ligated methylpalladium(II) alkoxides and aryl oxides, which includes the formation of O—H···O hydrogen-bonded adducts and alkynylpalladium(II) complexes. In this study, P,N-ligated palladium complexes have been prepared with variously substituted aryl oxide ligands to examine correlations of the ^{31}P NMR chemical shift and $^{3}J_{H,P}$ with various Hammet constants for the ring substituent.

Results and Discussion

Preparation of Methylpalladium(II) Alkoxide and Aryl Oxide Species 3-13. In previous papers from our laboratory, it has been shown that dimethylpalladium(II) complexes containing *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) easily undergo ligand exchange reactions.[13] Exchange of the tmeda in [Pd(Me)$_2$(tmeda)] for the P,N-chelating ligands *o*-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine (PCN) and (diphenylphosphino)-*N*,*N*-dimethylethyleneamine (PN) affords the known complex [Pd(Me)$_2$(PCN)] (**1**)[13a] and the new dimethylpalladium complex [Pd(Me)$_2$(PN)] (**2**) (see Figure 1), which have been used as starting materials for the preparation of new methylpalladium(II) alkoxide and aryl oxide complexes.

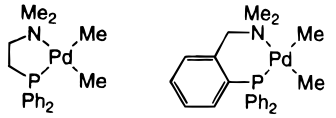
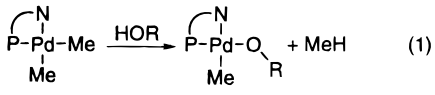


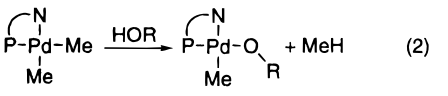
Figure 1. Schematic representation of the P,N-ligated complexes **1** and **2**.

Reaction of **1** with organic compounds ROH in a 1:1 molar ratio affords new complexes of the type [Pd(Me)(OR)(PN)] (**3**—**10**) (see eq 1). This reaction, in which CH_4 is the byproduct, has proved successful for 1,1,1,3,3,3-hexafluoro-2-propanol and the aryl alcohols HOC_6H_4-4-X (X = H, Cl, OMe, Me, CN, NO_2, OH). The methylpalladium(II) alkoxide and aryl oxide complexes **3**—**10** have been isolated in moderate-to-good yields as white or pale orange crystalline solids, which are thermally stable at room temperature. A similar reaction of [Pd(Me)$_2$(PCN)] (**2**) with 1 equiv of an aryl alcohol leads to the formation of aryl oxide and alkoxide complexes of the type [Pd(Me)(OR)(PCN)] (**11**—**13**) (see eq 2). By means of X-ray crystallography and NMR spectroscopy (*vide infra*), it has been unambiguously established that in these PN- and PCN-ligated complexes the alkoxide or aryl oxide ligand is positioned *trans* with respect to the P-donor atom.



P~N = PN

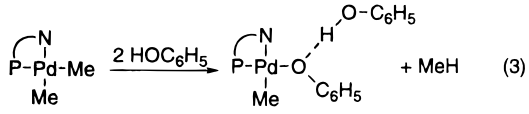
3: R = $CH(CF_3)_2$
4: R = C_6H_5
5: R = C_6H_4-4-OMe
6: R = C_6H_4-4-Me
7: R = C_6H_4-4-Cl
8: R = C_6H_4-4-CN
9: R = C_6H_4-4-NO_2
10: R = C_6H_4-4-OH



P~N = PCN

11: P~N = PCN, R = $CH(CF_3)_2$
12: P~N = PCN, R = C_6H_5
13: P~N = PCN, R = C_6H_4-4-CN

Reactivity of the PCN Complexes 2 and 4. The reaction of [Pd(Me)$_2$(PCN)] (**2**) with 2 equiv of phenol leads to the formation of an adduct formulated as [Pd(Me)(OC_6H_5)(PCN)]·HOC_6H_5 (**14**) (see eq 3). This alcohol-associated complex has been isolated as a yellow-orange crystalline solid (79%). The phenol-free complex **4**



14: P~N = PCN

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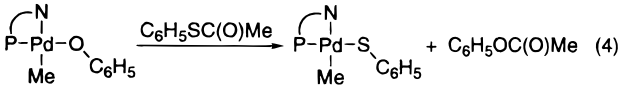
cannot be regenerated from adduct **14** by washing procedures, and this illustrates the stability of the O—H···O hydrogen bond in this adduct. By means of X-ray crystallography and NMR spectroscopy (*vide infra*), it has proved possible to unambiguously establish that adduct **14** has strong O—H···O hydrogen bonding both in the solid state and in solution. Analogous alcohol adducts of palladium alkoxide complexes containing bidentate N-donor ligands[11] and P-donor ligands[9] have been isolated as solids that are thermally stable at room temperature.

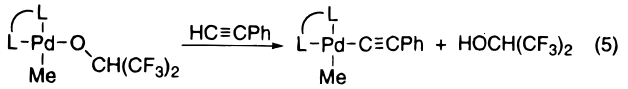
Reaction of [Pd(Me)(OC_6H_5)(PCN)] (**4**) with an equimolar amount of the thioester $C_6H_5SC(O)Me$ proceeds smoothly at room temperature to give the arenethiolate complex [Pd(Me)(SC_6H_5)(PCN)] (**15**), which has been isolated in 70% yield, and the carboxylic ester $C_6H_5OC(O)Me$ (see eq 4). Similar transesterification reactions



15: P~N = PCN

with methylpalladium alkoxide complexes containing mono- and bidentate P-donor ligands have been reported by Kim *et al.*[9e]

Reactivity of Alkoxide Complexes with Phenylacetylene. Reaction of the P,N-ligated palladium alkoxide complex [Pd(Me)($OCH(CF_3)_2$)(PN)] (**4**) with phenylacetylene produces the alkynyl complex [Pd(Me)(C≡CPh)(PN)] (**16**), which was isolated in 86% yield (see eq 5). To extend the scope of this reaction, we also used



16: L~L = PN
17: L~L = tmeda

the bidentate N-donor-ligated palladium alkoxide complex [Pd(Me)($OCH(CF_3)_2$)(tmeda)] as the starting material, and this species when treated with phenylacetylene affords the alkynyl complex [Pd(Me)(C≡CPh)(tmeda)] (**17**). The latter complex is not thermally stable in $CHCl_3$ solution, and above 0 °C it decomposes within a few minutes.

An interesting point is that the synthetic procedure for **16** and **17** does not give other alkynylpalladium(II) complexes, such as [Pd($OCH(CF_3)_2$)(C≡CPh)L_2] or [Pd(C≡CPh)$_2L_2$] (L_2 = PN or tmeda), that might be formed by protonation of the methyl ligand. Furthermore, insertion of the C≡C unit into the Pd—O bond does not occur, although several insertions of unsaturated compounds into M—O bonds have been reported.[15] We believe that the operative mechanism is probably concerted, with the driving force being the formation of the Pd—$C_{acetylide}$ bond; we consider an oxidative addition of phenylacetylene unlikely, and a nucleophilic substitution mechanism does not seem feasible since the pK_a values of PhC≡CH and hexafluoro-1-methylethanol are ca. 20 and 10, respectively. Thermolysis of **16** and **17** affords methylphenylacetylene as the only organic product (>98%) (see eq 6), whereas thermolysis of **16** and **17** in the presence of CO affords not only methylphenylacetylene but also small amounts (±3%) of the insertion product MeC(O)C≡CPh (see eq 7).

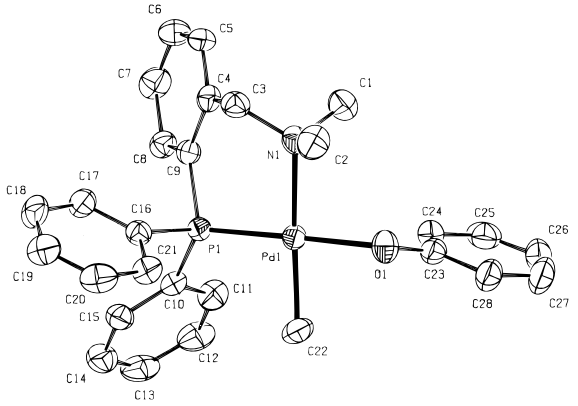


Figure 2. ORTEP (30% probability level) drawing of **12**. Hydrogen atoms and the dichloromethane solvate molecule are omitted for clarity.

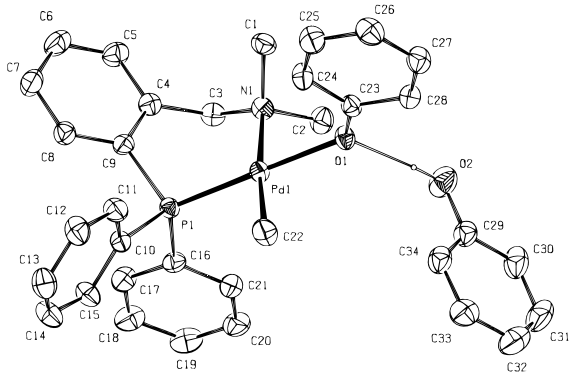
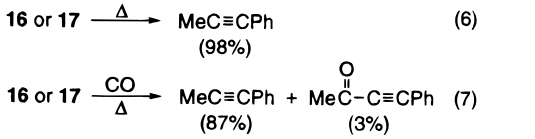


Figure 3. ORTEP (30% probability level) drawing of **14**. Hydrogen atoms are omitted for clarity.



Recently, it was reported that methylpalladium(II) alkynyl complexes with bidentate P-donor ligands can be formed by the reaction of methylpalladium(II) alkoxide complexes with acetylenes, and reductive elimination reactions of these alkynyl complexes were described.[14]

Molecular Structures of the PCN Methylpalladium Phenoxide Complex 12 and Its Phenol Adduct 14. Figures 2 and 3 show the molecular structures of [Pd(Me)(OC_6H_5)(PCN)] (**12**) and its phenol adduct [Pd(Me)(OC_6H_5)(PCN)]·HOC_6H_5 (**14**), respectively. The crystal structure of **12** also contains one non-coordinating dichloromethane solvate molecule in the asymmetric unit. Selected bond lengths and angles are summarized in Table 1.

Both **12** and **14** possess palladium atoms with an approximate square-planar coordination geometry, in which the phenoxide unit is positioned trans with respect to the P-atom. Adduct **14** shows the association of a phenol molecule to the phenoxide ligand through O—H···O hydrogen bonding (O···O = 2.624(5) Å, ∠O—H···O = 175(8)°). Hydrogen bonds can be considered

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Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for [Pd(Me)(OC_6H_5)(PCN)] (12) (CH_2Cl_2 Solvate) and Its Phenol Adduct [Pd(Me)(OC_6H_5)(PCN)]·HOC_6H_5 (14)[a]

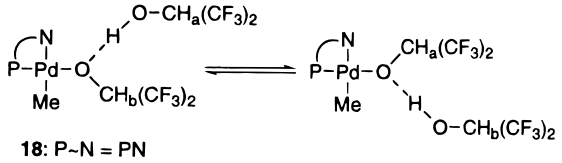
	12	14
	Bond Distances	
Pd—O(1)	2.088(5)	2.103(2)
Pd—C(22)	2.020(7)	2.024(5)
Pd—N(1)	2.205(5)	2.223(3)
Pd—P(1)	2.1900(16)	2.1949(11)
C(23)—O(1)	1.317(8)	1.318(4)
C(29)—O(2)		1.354(6)
O(1)···O(2)		2.624(5)
	Bond Angles	
Pd—O(1)—C(23)	122.6(4)	122.3(2)
P(1)—Pd—N(1)	92.19(13)	92.24(8)
P(1)—Pd—C(22)	92.3(2)	91.25(14)
P(1)—Pd—O(1)	178.87(15)	178.12(7)
N(1)—Pd—C(22)	173.8(2)	174.38(18)
O(2)—H···O(1)		175(8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

strong when the O···O distance falls in the range 2.50—2.65 Å for approximately linear O—H···O,[16] and on this basis we conclude that the hydrogen bond in **14** is reasonably strong. Furthermore, the O···O distance in **14** is comparable to O···O distances in both hydrogen-bonded organic molecules[17] and related palladium alkoxide and aryl oxide adducts.[9−11]

The molecular structure of **14** also reveals the presence of a possible electrostatic C—H···O interaction (not illustrated in Figure 3) of one NMe group with the oxygen of the palladium-bonded OC_6H_5 unit [C(2)···O(1) = 3.130(5) Å; C(2)—H(2B)···O(1) = 122(2)°]. Similar features not illustrated in Figure 2 are also present in the molecular structure of the dichloromethane adduct **12**. Namely, a close intramolecular contact between the NMe group and the oxygen atom of the phenoxide unit [C(2)···O(1) = 3.064(9) Å; C(2)—H(2B)···O(1) = 126(3)°] and close intermolecular contacts between the two dichloromethane methylene hydrogens and the oxygen atom of the phenoxide unit [C(29)···O(1) = 3.160(12) Å; C(29)—H(29A)···O(1) = 109.3(13) and C(29)—H(29B)···O(1) = 109.7(18)°]. We have reported earlier examples of C—H···O interactions in the N-ligated palladium alkoxide complexes [Pd($OCH(CF_3)_2$)(OC_6H_5)(bpy)]·HOC_6H_5[10b] and [Pd(Me)($OCH(CF_3)_2$)(tmeda)].[11a] One might conclude that this type of interaction is important in stabilizing late transition metal alkoxide or aryl oxide adducts and could be termed a steering interaction, which, although small in energy (4—8 kJ mol^{-1}), is sufficient to select a preferred molecular conformation.[18]

The Pd—O distances in **12** and **14** (2.088(5) and 2.103(2) Å, respectively) are longer than the Pd—O distances that we have found in the related N-donor-ligated complex [Pd(Me)(OC_6H_5)(tmeda)] and its HOC_6H_5 adduct (2.024(3) and 2.037(2) Å, respectively).[11a] It is the presence of a P-donor atom trans to the phenoxide unit that is probably the most important reason for this lengthening. Association of a phenol causes a further lengthening of the Pd—O bond by ∼0.015(5) Å; similar elongations of the Pd—O bond upon phenol adduct formation have been reported by ourselves for [Pd(Me)(OC_6H_4X-4)(tmeda)] (X = H, NO_2)[11a] and by others for *trans*-[Pd(Me)(OC_6H_5)(PMe_3)$_2$].[9e]



18: P~N = PN

Figure 4. Intramolecular exchange of coordinated alkoxide and associated alcohol.

Solution Behavior of PN Alkoxide Complexes 2 and 18. Addition of 1 equiv of $HOCH(CF_3)_2$ to the alkoxide complex [Pd(Me)($OCH(CF_3)_2$)(PN)] (**2**) in toluene leads to the *in situ* formation of an O—H···O hydrogen-bonded adduct [Pd(Me)($OCH(CF_3)_2$)(PN)]·$HOCH(CF_3)_2$ (**18**), but so far it has not proved possible to isolate this adduct as a solid (see Experimental Section). The ^{1}H NMR spectrum of adduct **18** formed *in situ* in toluene-d_8 (25 °C) shows the OH hydrogen of the associated alcohol at 8.05 ppm, and such a low-field position is characteristic for a transition metal alcohol adduct.[9,11] Further, the spectrum shows, at 4.65 ppm, *one* well-resolved septet corresponding to the OC*H* hydrogens of both the fluorinated alkoxide unit (Pd—OR) and the associated alcohol (ROH). Cooling of this solution of **18** to 200 K causes this resonance to split into two separate OC*H* signals for the alkoxide and the alcohol unit at δ 4.73 and 4.90, respectively; the coalescence temperature is ±243 K, with $\Delta G^{\#}$ of ca. 12 kcal mol^{-1}. This behavior can be explained by an intramolecular exchange of coordinated alkoxide and associated alcohol, as illustrated in Figure 4, which is fast on the NMR time scale at room temperature. Unfortunately, we were not able to determine the detailed thermodynamic parameters for this alkoxide—alcohol exchange in **18** due to the small separation of ±50 Hz for the OC*H* hydrogens of the alkoxide and alcohol units at low temperature.

Kim *et al*. found for [Pd(Me)($OCH(CF_3)(Ph)$)(PMe_3)$_2$]·$HOCH(CF_3)(Ph)$ (an adduct with phosphine ligands that bears analogy to adduct **18**) that the OC*H* hydrogens of the alkoxide and alcohol coalesce at 273 K, and their conclusion, based upon thermodynamic data, likewise is that an intramolecular alkoxide—alcohol exchange mechanism is operative.[9e] We and others have studied the temperature dependence of the OH hydrogen for these alcohol adducts of palladium alkoxides and aryl oxides (i.e., measurement of palladium alkoxide—alcohol association equilibria), and it was possible to quantify the O—H···O hydrogen bond in palladium alkoxide adducts as strong ($\Delta H°$ = 20—34 kJ mol^{-1}).[9a,e,10a,11a]

Solution Behavior of PCN Complexes 11 and 12. ^{1}H NMR spectra (benzene-d_6) of the PCN complexes [Pd(Me)($OCH(CF_3)_2$)(PCN)] (**11**) and [Pd(Me)(OC_6H_5)(PCN)] (**12**) at 300 K show broad resonances at approximately δ 2.80 and 2.40, assigned to the NCH_2 and NMe_2 groups, respectively. Models of these complexes show that because of chelate ring puckering the two *N*-methyl groups, the benzylic protons, and the PPh_2 phenyl groups are diastereotopic. Upon cooling of solutions of **11** and **12** in toluene-d_8, the resonance of the NMe_2

(16) Gille, P.; Bertolasi, V.; Ferritti, V.; Gilli, G. *J. Am. Chem. Soc.* **1994**, *116*, 909.

(17) (a) Schuster, P., Zundel, G., Sandorfy, C., Eds.; *The Hydrogen Bond*; North Holland: Amsterdam, 1976. (b) Joesten, M. D.; Schaad, L. J. *Hydrogen Bonding*; Marcel Dekker: New York, 1974. (c) Pimentel, G. C.; McLellan, A. L. *The Hydrogen Bond*; W. H. Freeman: San Francisco, CA, 1960.

(18) (a) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290. (b) Chloroform and dichloromethane can form C—H···O bonds, see: Green, R. D. *Hydrogen Bonding in C-H Groups*; MacMillan: London, 1974.

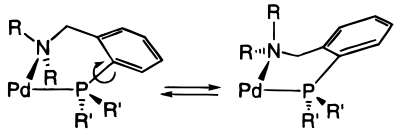


Figure 5. Conformational interconversion of the coordinated PCN ligand.

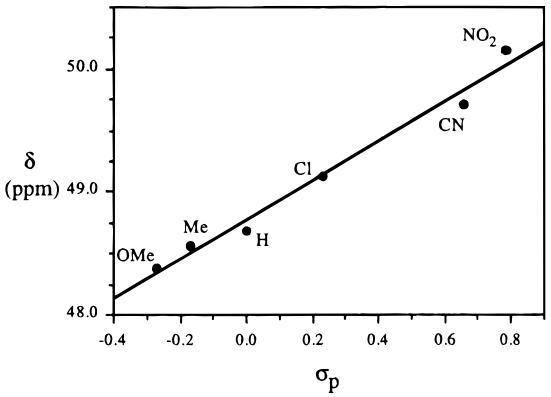


Figure 6. Plot of ^{31}P chemical shift versus σ_p. For data see Table 2.

Table 2. NMR Spectral Data for Para-Substituted Aryl Oxide Complexes [Pd(Me)(OC$_6$H$_4$X-4)(PN)] (4−10)[a]

complex	X	$^3J_{H,P}$ (Hz)[b]	^{31}P (ppm)
4	H	2.48	48.68
5	OMe	2.55	48.39
6	Me	2.55	48.56
7	Cl	2.39	49.13
8	CN	2.17	49.71
9	NO_2	2.01	50.15
10	OH	2.71	

[a] Measured in CD_3COCD_3. [b] PdMe group (±0.07 Hz).

group splits into two lines ($\Delta\delta$ = 78 Hz, $\Delta G^{\#}$ = 10 kcal mol^{-1}). We believe that this temperature dependent behavior is a consequence of the conformational interconversion shown in Figure 5, which may be described as resulting from a partial rotation (wagging) of the aromatic ring around the P−Ar bond axis. Rauchfuss *et al*. reported a similar fluxional behavior of the PCN ligand in the complex [RhCl(CO)(PCN)], for which an activation energy of 8.8 kcal mol^{-1} was calculated.[19]

Correlation of NMR Data with Hammet Substituent Constants. Relevant ^{31}P NMR chemical shift data and values of $^3J_{H,P}$ for the PdMe group positioned cis to the P-donor atom in the palladium aryl oxide complexes [Pd(Me)(OC$_6$H$_4$-4-X)(PN)] (**4**−**10**) are summarized in Table 2. The plot and line fitting for the ^{31}P NMR shift and $^3J_{H,P}$ versus the Hammet constant σ_p (see Figures 6 and 7, respectively) show that more electron-withdrawing *para* substituents result in an increase of the δ ^{31}P and a decrease in $^3J_{H,P}$. To obtain more detailed insight, we have correlated our NMR data (δ ^{31}P NMR and $^3J_{H,P}$) for the complexes **4**−**10** versus several specific substituent constants,[20] and the corresponding correlation coefficients obtained are shown in Table 3.

Examination of both NMR data sets shows that the best linearity is obtained for the σ_p and σ_p^- parameters.

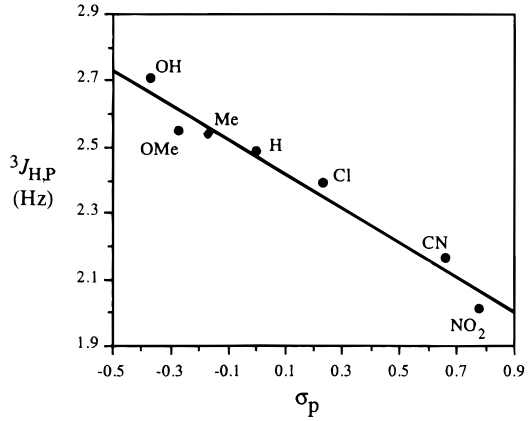


Figure 7. Plot of $^3J_{H,P}$ versus σ_p. For data see Table 2.

Table 3. Correlation Coefficients for Hammett Substituent Parameters with NMR Spectral Data

substituent constant	correlation coefficient	
	δ ^{31}P	$^3J_{H,P}$
σ_p	0.98	0.96
σ_p^+	0.90	0.89
σ_p^-	0.98	0.97
F	0.73	0.50
R	0.61	0.70

This result indicates that the sum of resonance and inductive/field effects of the substituent directly influence the two chosen NMR parameters. The Hammet constant σ_p^-, which reflects the effect that a ring substituent has on a reaction that results in an increase in negative charge in the transition state, exhibits a good correlation with the ^{31}P NMR shift and $^3J_{H,P}$ (see Table 3). This is logical since the aromatic ring of the aryl oxide in these complexes has anionic character, and one also sees a low correlation of ^{31}P NMR shift and $^3J_{H,P}$ with the Hammet constant σ_p^+. The poor correlations obtained for the Taft field and resonance constants, F and R, again emphasize that it is a combination of both resonance and inductive/field effects that influences the NMR parameters. Although the influence of the *para* substituents is not large, the preceding results can be explained with a simple model. In this model, the electron-donating substituents on the aryl oxide unit increase the net negative charge on the aromatic ring, which shifts some of the increased charge to the palladium atom.[20] This extra negative charge placed on the metal is now available for donation to the π*-orbital of the P-atom, and this results in a high-field shift in ^{31}P NMR. This increase in electron density between P and Pd is probably also the cause of an increase in $^3J_{P,H}$.

Concluding Remarks. The results presented in this paper illustrate that bidentate P,N-donor ligands are suitable for stabilizing methylpalladium(II) species with alkoxide or aryl oxide ligands and that these species have a strong tendency to form adducts with alcohols. These new alkoxide complexes furthermore are useful starting materials for the preparation of alkynyl and thiolate palladium(II) complexes. Further studies are in progress to investigate the potential of these complexes in synthetic studies and catalytic processes.

Experimental Section

General Considerations. Reactions were performed in an atmosphere of nitrogen using standard Schlenk techniques.

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(20) Hansch, C.; Leo, A.; Taft, W. R. *Chem. Rev*. **1991**, *91*, 165.
(21) Blais, M. S.; Rausch, M. D. *Organometallics* **1994**, *13*, 3557.

C_6H_6, Et_2O, and pentane were freshly distilled from sodium benzophenone ketyl. CH_2Cl_2 was distilled from CaH_2. All other solvents were used as received. The solvent acetone (p.a.) and the materials 1,1,1,3,3,3-hexafluoro-2-propanol, HOC_6H_4-4-X (X = H, NO_2, OH, CN, Cl, Me, OMe), catechol, and Celite (filter aid) were purchased from Janssen Chimica. The compounds $Ph_2PCH_2CH_2NMe_2$ (PN),[22] [Pd(Me)$_2$(tmeda)],[13a] [Pd(Me)$_2$(PCN)] (**1**),[13a] and [Pd(Me)(OCH(CF$_3$)$_2$)(tmeda)][11] were prepared according to the literature. ^{1}H (300.13 MHz), ^{13}C (75.04 MHz), and ^{31}P (121.47 MHz) NMR spectra were recorded on a Bruker AC 300 spectrometer at ambient temperature in deuterated solvents ($CDCl_3$, C_6D_6, CD_3COCD_3, and toluene-d_8) obtained from ISOTEC Inc. NMR data for the Hammet correlation have been obtained by using the same measurement conditions (solvent CD_3COCD_3, temperature 298 K, and concentration 0.015 M) to minimize errors. Elemental analyses were carried out by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

Preparation of [Pd(Me)$_2$(PN)] (2). To a solution of [Pd(Me)$_2$(tmeda)] (0.94 g, 3.72 mmol) in benzene (20 mL) was added a solution of PN (1.00 g, 3.88 mmol) in a mixture of benzene (5 mL) and pentane (40 mL). The resulting yellow solution was stirred for 3 h, during which time a white precipitate of the product was formed. The solid was isolated by decantation, washed with pentane (2 × 5 mL), and dried *in vacuo*. The product can be crystallized from slow diffusion of pentane into a solution of benzene: yield 1.23 g (84%); ^{1}H NMR (CD_3COCD_3) δ 7.75−7.21 (m, 10H, aryl), 2.63−2.40 (m, 4H, CH_2CH_2), 2.52 (s, 6H, N(CH_3)$_2$), 0.25 (d, 3H, $^3J_{H,P}$ = 7.8 Hz, PdCH_3), −0.38 (d, 3H, $^3J_{H,P}$ = 7.2 Hz, PdCH_3). Anal. Calcd for $C_{18}H_{20}NOPPd\cdot0.5C_6H_6$: C, 58.27; H, 6.75; N, 3.24. Found: C, 57.95; H, 6.53; N, 3.15.

Preparation of [Pd(Me)(OCH(CF$_3$)$_2$)(PN)] (3). To a solution of [Pd(Me)$_2$(PN)] (**2**) (0.81 g, 2.1 mmol) in benzene (20 mL) was added 1,1,1,3,3,3-hexafluoro-2-propanol (216 μL, 2.1 mmol). After 2 h the yellow solution was reduced *in vacuo* to half its volume. The addition of pentane (25 mL) afforded a white precipitate, which was isolated by decantation, washed with pentane (4 × 5 mL), and dried *in vacuo*. The product can be recrystallized from toluene, yielding colorless crystals: yield 0.90 g (80%); ^{1}H NMR (CD_3COCD_3) δ 7.79−7.63 (m, 4H, aryl), 7.60−7.48 (m, 6H, aryl), 4.48 (septet, 1H, $^3J_{H,F}$ = 6.5 Hz, OCH), 2.75−2.50 (m, 4H, CH_2CH_2), 2.60 (s, 6H, NCH_3), 0.15 (d, 3H, $^3J_{H,P}$ = 1.2 Hz, PdCH_3); ^{13}C NMR (CD_3COCD_3) δ 134.09 (d, $^2J_{C,P}$ = 12 Hz, *m*-*C* aryl), 132.02 (*p*-*C* aryl), 131.42 (d, $^1J_{C,P}$ = 50 Hz, ipso-*C* aryl), 129.80 (d, $^3J_{C,P}$ = 11 Hz, *o*-C aryl), 125.62 (q, $^1J_{C,F}$ = 286 Hz), 74.98 (septet, $^2J_{C,F}$ = 29 Hz, O*C*H), 59.34 (d, $^2J_{C,P}$ = 5 Hz, NCH_2), 47.48 (NCH_3), 31.35 (d, $^1J_{C,P}$ = 12 Hz, PCH_2), −3.24 (d, $^2J_{C,P}$ = 7.5 Hz, PdCH_3). Anal. Calcd for $C_{20}H_{24}F_6NOPPd$: C, 44.01; H, 4.43; N, 2.57. Found: C, 44.16; H, 4.42; N, 2.67.

Preparation of [Pd(Me)(OC$_6$H$_5$)(PN)] (4). To a solution of [Pd(Me)$_2$(PN)] (**2**) (0.70 g, 1.8 mmol) in benzene (10 mL) ws added a solution of phenol (0.17 g, 1.8 mmol) in a mixture of benzene (5 mL) and pentane (20 mL). After 1 h, the white precipitate that had formed was isolated by decantation, washed with pentane (3 × 30 mL), and dried *in vacuo*: yield 0.76 g (91%); ^{1}H NMR (CD_3COCD_3) δ 7.85−7.76 (m, 4H, aryl), 7.62−7.52 (m, 6H, aryl), 6.89 (t, 2H, $^3J_{H,H}$ = 8 Hz, *o*-*H* PdOAr), 6.72 (d, 2H, $^3J_{H,H}$ = 8 Hz, *m*-*H* PdOAr), 6.23 (t, 1H, $^3J_{H,H}$ = 8 Hz, *p*-*H* PdOAr), 2.80−2.72 (m, 2H, CH_2), 2.63−2.50 (m, 2H, CH_2), 2.61 (s, 6H, NCH$_3$), 0.33 (d, 3H, $^3J_{H,P}$ = 2.48 Hz, PdCH_3); ^{13}C NMR (CD_3COCD_3) δ 134.12 (d, $^2J_{C,P}$ = 12 Hz, *m*-*C* aryl), 131.91 (*p*-*C* aryl), 131.70 (d, $^1J_{C,P}$ = 50 Hz, ipso-*C* aryl), 129.80 (d, $^3J_{C,P}$ = 10 Hz, *o*-*C* aryl), 129.22 (*m*-*H* PdOAr), 121.14 (*o*-*H* PdOAr), 112.21 (*p*-*H* PdOAr), 59.15 (d, $^2J_{C,P}$ = 5 Hz, NCH_2), 48.14 (NCH$_3$), 31.15 (d, $^1J_{C,P}$ = 29 Hz, PCH_2), −4.86 (d, $^2J_{C,P}$ = 6.6 Hz, PdCH_3); ^{31}P{^{1}H} NMR (CD_3COCD_3) δ 48.68. Anal. Calcd for $C_{23}H_{28}NOPPd$: C, 58.54; H, 5.98; N, 2.97. Found: C, 58.52; H, 5.93; N, 2.91.

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Preparation of [Pd(Me)(OC$_6$H$_4$-4-OMe)(PN)] (5). To a solution of [Pd(Me)$_2$(PN)] (**2**) (0.30 g, 0.76 mmol) in a mixture of benzene (3 mL) and Et_2O (3 mL) was added a solution of anisole (0.046 g, 0.78 mmol) in benzene (5 mL). After 10 min, the white precipitate was isolated by decantation, washed with pentane (3 × 30 mL), and dried *in vacuo*: yield 0.26 g (69%); ^{1}H NMR (CD_3COCD_3) δ 7.83−7.76 (m, 4H, aryl), 7.59−7.52 (m, 6H, aryl), 6.65 (d, 2H, $^3J_{H,H}$ = 9 Hz, *o*-*H* PdOAr), 6.55 (d, 2H, $^3J_{H,H}$ = 9 Hz, *m*-*H* PdOAr), 3.61 (s, 3H, OCH$_3$), 2.79−2.72 (m, 2H, CH_2), 2.62−2.50 (m, 2H, CH_2), 2.61 (s, 6H, NCH_3), 0.31 (d, 3H, $^3J_{H,P}$ = 2.55 Hz, PdCH_3); ^{13}C NMR (CD_3COCD_3) δ 169.66 (ipso-*C* PdOAr), 134.11 (d, $^2J_{C,P}$ = 12 Hz, *m*-*C* aryl), 131.98 (d, $^1J_{C,P}$ = 50 Hz, ipso-*C* aryl), 131.95 (*p*-*C* aryl), 129.82 (d, $^3J_{C,P}$ = 11 Hz, *o*-*C* aryl), 129.10 (*m*-*H* PdOAr), 120.64 (*p*-*H* PdOAr), 115.31 (*o*-*H* PdOAr), 59.25 (NCH_2), 56.26 (OCH_3), 48.31 (NCH_3), 31.13 (d, $^1J_{C,P}$ = 29 Hz, PCH_2), −4.23 (d, $^2J_{C,P}$ = 6.0 Hz, PdCH_3); ^{31}P{^{1}H} NMR (CD_3COCD_3) δ 48.39. Anal. Calcd for $C_{24}H_{30}NO_2PPd$: C, 57.43; H, 6.03; N, 2.79. Found: C, 57.36; H, 6.00; N, 2.73.

Preparation of [Pd(Me)(OC$_6$H$_4$-4-Me)(PN)] (6). To a solution of [Pd(Me)$_2$(PN)] (**2**) (0.162 g, 0.42 mmol) in benzene (5 mL) was added a solution of *p*-cresol (0.048 g, 0.44 mmol) in Et_2O (20 mL). After 30 min, the beige precipitate that had formed was isolated by decantation, washed with pentane (3 × 30 mL), and dried *in vacuo*: yield 0.13 g (65%); ^{1}H NMR (CD_3COCD_3) δ 7.84−7.77 (m, 4H, aryl), 7.59−7.53 (m, 6H, aryl), 6.71 (d, 2H, $^3J_{H,H}$ = 8 Hz, *o*-*H* PdOAr), 6.63 (d, 2H, $^3J_{H,H}$ = 8 Hz, *m*-*H* PdOAr), 2.78−2.70 (m, 2H, CH_2), 2.64−2.49 (m, 2H, CH_2), 2.61 (s, 6H, NCH_3), 2.10 (s, 3H, OArCH_3), 0.32 (d, 3H, $^3J_{H,P}$ = 2.55 Hz, PdCH_3); ^{13}C NMR (CD_3COCD_3) δ 168.70 (ipso-*C* PdOAr), 134.12 (d, $^2J_{C,P}$ = 12 Hz, *m*-*C* aryl), 131.94 (d, $^1J_{C,P}$ = 50 Hz, ipso-*C* aryl), 131.92 (*p*-*C* aryl), 129.86 (d, $^3J_{C,P}$ = 11 Hz, *o*-*C* aryl), 129.82 (*m*-*H* PdOAr), 120.80 (*o*-*H* PdOAr), 120.04 (*p*-*H* PdOAr), 59.15 (d, $^2J_{C,P}$ = 5 Hz, NCH_2), 48.13 (NCH_3), 31.14 (d, $^1J_{C,P}$ = 29 Hz, PCH_2), 20.60 (OAr*C*H$_3$), −4.64 (d, $^2J_{C,P}$ = 6.8 Hz, PdCH_3); ^{31}P{^{1}H} NMR (CD_3COCD_3) δ 48.56. Anal. Calcd for $C_{24}H_{30}NOPPd$: C, 59.33; H, 6.22; N, 2.88. Found: C, 59.21; H, 6.28; N, 2.93.

Preparation of [Pd(Me)(OC$_6$H$_4$-4-Cl)(PN)] (7). To a solution of [Pd(Me)$_2$(PN)] (**2**) (0.151 g, 0.38 mmol) in benzene (5 mL) was added a solution of *p*-chlorophenol (0.049 g, 0.38 mmol) in Et_2O (10 mL). After 30 min, the white precipitate that had formed was isolated by decantation, washed with Et_2O (5 mL) and pentane (3 × 30 mL), and dried *in vacuo*: yield 0.17 g (88%); ^{1}H NMR (CD_3COCD_3) δ 7.84−7.77 (m, 4H, aryl), 7.60−7.55 (m, 6H, aryl), 6.85 (d, 2H, $^3J_{H,H}$ = 8 Hz, *o*-*H* PdOAr), 6.67 (d, 2H, $^3J_{H,H}$ = 8 Hz, *m*-*H* PdOAr), 2.79−2.73 (m, 2H, CH_2), 2.66−2.53 (m, 2H, CH_2), 2.61 (s, 6H, NCH_3), 0.30 (d, 3H, $^3J_{H,P}$ = 2.39 Hz, PdCH_3); ^{13}C NMR (CD_3COCD_3) δ 167.12 (ipso-*C* PdOAr), 134.21 (d, $^2J_{C,P}$ = 12 Hz, *m*-*C* aryl), 132.02 (*p*-*C* aryl), 131.55 (d, $^1J_{C,P}$ = 50 Hz, ipso-*C* aryl), 129.83 (d, $^3J_{C,P}$ = 11 Hz, *o*-*C* aryl), 128.88 (*m*-*H* PdOAr), 122.11 (*o*-*H* PdOAr), 119.80 (*p*-*H* PdOAr), 59.13 (d, $^2J_{C,P}$ = 5 Hz, NCH_2), 48.13 (NCH_3), 31.15 (d, $^1J_{C,P}$ = 29 Hz, PCH_2), −4.82 (d, $^2J_{C,P}$ = 6.7 Hz, PdCH_3); ^{31}P{^{1}H} NMR (CD_3COCD_3) δ 49.13. Anal. Calcd for $C_{23}H_{27}ClNOPPd$: C, 54.56; H, 5.38; N, 2.77. Found: C, 54.41; H, 5.29; N, 2.77.

Preparation of [Pd(Me)(OC$_6$H$_4$-4-CN)(PN)] (8). To a solution of [Pd(Me)$_2$(PN)] (**2**) (0.118 g, 0.30 mmol) in Et_2O (5 mL) was added a solution of *p*-cyanophenol (0.036 g, 0.30 mmol) in a mixture of Et_2O (5 mL) and benzene (5 mL). After 30 min, pentane (15 mL) was added and an orange precipitate formed that was isolated by decantation, washed with pentane (2 × 10 mL), and dried *in vacuo*: yield 0.13 g (87%); ^{1}H NMR (CD_3COCD_3) δ 7.85−7.78 (m, 4H, aryl), 7.62−7.55 (m, 6H, aryl), 7.24 (d, 2H, $^3J_{H,H}$ = 8 Hz, *o*-*H* PdOAr), 6.77 (d, 2H, $^3J_{H,H}$ = 8 Hz, *m*-*H* PdOAr), 2.85−2.78 (m, 2H, CH_2), 2.72−2.63 (m, 2H, CH_2), 2.60 (s, 6H, NCH_3), 0.29 (d, 3H, $^3J_{H,P}$ = 2.17 Hz, PdCH_3); ^{13}C NMR (CD_3COCD_3) δ 175.25 (ipso-*C* PdOAr), 134.17 (d, $^2J_{C,P}$ = 12 Hz, *m*-*C* aryl), 133.90 (*m*-*H* PdOAr), 132.20 (*p*-*C* aryl), 131.06 (d, $^1J_{C,P}$ = 50 Hz, ipso-*C* aryl), 129.93 (d, $^3J_{C,P}$ = 11 Hz, *o*-*C* aryl), 122.31 (*p*-*H* PdOAr), 121.90 (*o*-*H*

Table 4. Crystallographic Data for 12 and 14

	12	14
	Crystal Data	
formula	$C_{28}H_{30}NOPPd\cdot CH_2Cl_2$	$C_{28}H_{30}NOPPd\cdot C_6H_6O$
molecular weight	618.88	628.06
crystal system	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	8.2903(9)	10.903(3)
b (Å)	11.5330(13)	11.763(2)
c (Å)	16.0124(15)	12.598(2)
α (deg)	102.641(8)	76.806(11)
β (deg)	90.736(8)	83.366(15)
γ (deg)	105.567(9)	71.733(15)
V (Å^3)	1434.9(3)	1492.1(6)
D_{calc} (g cm^{-3})	1.432	1.398
Z	2	2
F(000)	632	648
μ (cm^{-1})	9.0 (Mo Kα)	58.8 (Cu Kα)
crystal size (mm)	0.7 × 0.5 × 0.2	0.5 × 0.5 × 0.2
	Data Collection	
T (K)	298	295
θ_{min}, θ_{max} (deg)	1.31, 25.48	3.61, 74.99
wavelength (Å)	0.71073 (Mo Kα, Zr-filtered)	1.54184 (Cu Kα, Ni-filtered)
scan type	$\omega/2\theta$	$\omega/2\theta$
$\Delta\omega$ (deg)	0.94 + 0.35 tan θ	0.71 + 0.14 tan θ
hor., ver. aperture (mm)	3.17, 5.00	4.18, 6.00
X-ray exposure time	80	101
linear decay (%)	81	10
reference reflections	$\bar{2}1\bar{4}$,$\bar{2}23$,$14\bar{2}$	$\bar{2}32$,$\bar{1}2\bar{4}$,052
data set	−9:9,0:13,−19:18	−13:13,−14:14,−15:15
total data	5518	12641
total unique data	5236 (R_{int} = 0.045)	6125 (R_{int} = 0.037)
DIFABS corr range	0.759, 1.191	0.686, 1.951
	Refinement	
no. of refined params	319	359
final R^a	0.062 [3467 $F_o > 4\sigma(F_o)$]	0.039 [5446 $F_o > 4\sigma(F_o)$]
final $wR2^b$	0.167	0.114
goodness of fit	1.04	1.11
weighting scheme^c	$[\sigma^2(F^2) + (0.1026P)^2]^{-1}$	$[\sigma^2(F^2) + (0.0466P)^2 + 2.39P]^{-1}$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.000, −0.001	0.000, −0.004
min and max residual density (e Å^{-3})	−0.86, 0.68	−1.30, 1.09 (near Pd)

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

PdOAr), 59.08 (d, $^2J_{C,P}$ = 5 Hz, NCH_2), 48.24 (NCH_3), 31.20 (d, $^1J_{C,P}$ = 29 Hz, PCH_2), −5.05 (d, $^2J_{C,P}$ = 6.1 Hz, $PdCH_3$); $^{31}P\{^1H\}$ NMR (CD_3COCD_3) δ 49.71. Anal. Calcd for $C_{24}H_{27}N_2OPPd$: C, 58.01; H, 5.48; N, 5.64. Found: C, 58.09; H, 5.53; N, 5.71.

Preparation of [Pd(Me)(OC$_6$H$_4$-4-NO$_2$)(PN)] (9). To a solution of $[Pd(Me)_2(PN)]$ (**2**) (0.271 g, 0.69 mmol) in benzene (5 mL) was added a solution of *p*-nitrophenol (0.097 g, 0.70 mmol) in a mixture of Et_2O (10 mL) and pentane (5 mL). After 15 min, a yellow precipitate formed that was isolated by decantation, washed with pentane (2 × 20 mL), and dried *in vacuo*: yield 0.28 g (85%); ^1H NMR (CD_3COCD_3) δ 7.94 (d, 2H, $^3J_{H,H}$ = 8 Hz, *o-H* PdOAr), 7.93−7.81 (m, 4H, aryl), 7.62−7.55 (m, 6H, aryl), 6.72 (d, 2H, $^3J_{H,H}$ = 8 Hz, *m-H* PdOAr), 2.85−2.60 (m, 4H, CH_2CH_2), 2.60 (s, 6H, NCH_3), 0.30 (d, 3H, $^3J_{H,P}$ = 2.01 Hz, $PdCH_3$); $^{31}P\{^1H\}$ NMR (CD_3COCD_3) δ 50.15. Anal. Calcd for $C_{23}H_{27}N_2O_3PPd$: C, 53.45; H, 5.27; N, 5.42. Found: C, 53.34; N, 5.36; N, 5.48.

Preparation of [Pd(Me)(OC$_6$H$_4$-4-OH)(PN)] (10). To a solution of $[Pd(Me)_2(PN)]$ (**2**) (0.186 g, 0.52 mmol) in Et_2O (5 mL) was added a solution of hydroquinone (0.052 g, 0.52 mmol) in a mixture of Et_2O (5 mL) and benzene (2 mL). After the solution was warmed to 35 °C for 15 min, a white precipitate formed that was isolated by decantation, washed with Et_2O (2 × 5 mL), and dried *in vacuo*: yield 0.19 g (81%); ^1H NMR (CD_3COCD_3) δ 8.02−7.10 (m, 14H, aryl), 2.69−2.48 (m, 4H, CH_2CH_2), 2.63 (s, 6H, NCH_3), 0.81 (d, 3H, $^3J_{H,P}$ = 2.71 Hz, $PdCH_3$).

Preparation of [Pd(Me)(OCH(CF$_3$)$_2$)(PCN)] (11). To a solution of $[Pd(Me)_2(PCN)]$ (**1**) (0.089 g, 0.020 mmol) in benzene (7 mL) was added 1,1,1,3,3,3-hexafluoro-2-propanol (21 μL, 0.021 mmol). The solution turned yellow and a precipitate formed. After 1 h the suspension was evaporated to dryness *in vacuo*, and the residue was washed with pentane (3 × 10 mL) and dried *in vacuo*: yield 0.110 g (93%); ^1H NMR (C_6D_6) δ 7.41−6.69 (m, 14H, aryl), 5.05 (septet, 1H, $^3J_{H,F}$ = 6.5 Hz, OC*H*), 2.84 (br m, 2H, CH_2), 2.42 (br m, 6H, NCH_3), 0.61 (d, 3H, $^3J_{H,P}$ = 2.2 Hz, $PdCH_3$). Anal. Calcd for $C_{25}H_{26}F_6NOPPd$: C, 49.40; H, 4.31; N, 2.30. Found: C, 48.66; H, 4.46; N, 2.47.

Preparation of [Pd(Me)(OC$_6$H$_5$)(PCN)] (12). To a solution of $[Pd(Me)_2(PCN)]$ (**1**) (0.63 g, 0.14 mmol) in benzene (10 mL) was added a solution of phenol (0.13 g, 0.14 mmol) in a mixture of benzene (5 mL) and Et_2O (20 mL). A white precipitate formed, which was isolated after 1 h by decantation, washed with Et_2O (25 mL), and dried *in vacuo*. The product can be crystallized by slow diffusion of pentane into a CH_2Cl_2 solution, affording yellow crystals suitable for X-ray diffraction: yield 0.61 g (81%); ^1H NMR (C_6D_6) δ 7.87−6.79 (m, 18H, aryl), 6.57 (t, 1H, $^3J_{H,H}$ = 7 Hz, *p*-H PdOPh), 2.86 (br m, 2H, CH_2), 2.37 (br s, 6H, NCH_3), 0.97 (d, 3H, $^3J_{H,P}$ = 3.3 Hz, $PdCH_3$); ^{13}C NMR ($CDCl_3$) δ 141.81, 134.39, 134.23, 132.83, 132.71, 131.08, 130.94, 129.23, 129.15, 128.89, 128.45, 127.68, 120.37, 112.73, 66.46 (d, $^2J_{C,P}$ = 9.4 Hz, CH_2), 48.25 (NCH_3), 2.13 (d, $^2J_{C,P}$ = 5.5 Hz, $PdCH_3$). Anal. Calcd for $C_{28}H_{30}NOPPd$: C, 62.99; H, 5.66; N, 2.62. Found: C, 62.78; H, 5.74; N, 2.66.

Preparation of [Pd(Me)(OC$_6$H$_4$-4-CN)(PCN)] (13). To a solution of $[Pd(Me)_2(PCN)]$ (**1**) (0.0965 g, 0.210 mmol) in Et_2O (5 mL) was added a solution of *p*-cyanophenol (0.0252 g, 0.210

Table 5. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for 12 (esd's in Parentheses)[a]

atom	*x*	*y*	*z*	U_{eq} (Å^2)[a]
Pd(1)	0.82149(5)	0.15967(4)	0.25480(3)	0.0494(2)
P(1)	0.9740(2)	0.34281(13)	0.24525(10)	0.0467(5)
O(1)	0.6718(6)	−0.0139(4)	0.2635(3)	0.0683(16)
N(1)	1.0218(6)	0.0734(4)	0.2102(3)	0.0588(19)
C(1)	0.9612(9)	−0.0163(6)	0.1270(5)	0.084(3)
C(2)	1.0479(9)	0.0063(7)	0.2753(6)	0.086(3)
C(3)	1.1877(7)	0.1579(6)	0.2010(4)	0.063(2)
C(4)	1.1848(7)	0.2366(5)	0.1377(4)	0.0545(19)
C(5)	1.2751(8)	0.2238(6)	0.0651(5)	0.073(3)
C(6)	1.2828(9)	0.2982(7)	0.0086(5)	0.079(3)
C(7)	1.1963(9)	0.3857(7)	0.0211(4)	0.077(3)
C(8)	1.1006(7)	0.3985(6)	0.0933(4)	0.059(2)
C(9)	1.0960(6)	0.3273(5)	0.1508(4)	0.0485(17)
C(10)	0.8676(6)	0.4586(5)	0.2336(4)	0.050(2)
C(11)	0.7287(8)	0.4232(6)	0.1751(5)	0.068(3)
C(12)	0.6426(9)	0.5066(8)	0.1644(5)	0.084(3)
C(13)	0.6924(11)	0.6257(8)	0.2153(6)	0.087(4)
C(14)	0.8264(9)	0.6600(6)	0.2747(5)	0.079(3)
C(15)	0.9115(8)	0.5749(5)	0.2840(4)	0.064(2)
C(16)	1.1323(7)	0.4224(5)	0.3317(4)	0.053(2)
C(17)	1.2798(8)	0.5061(6)	0.3207(4)	0.068(2)
C(18)	1.3920(8)	0.5754(7)	0.3896(5)	0.082(3)
C(19)	1.3571(9)	0.5581(8)	0.4708(5)	0.083(3)
C(20)	1.2162(10)	0.4739(8)	0.4820(5)	0.080(3)
C(21)	1.1018(8)	0.4045(6)	0.4138(4)	0.062(2)
C(22)	0.6344(8)	0.2276(6)	0.3053(5)	0.075(3)
C(23)	0.5406(7)	−0.0766(5)	0.2095(5)	0.058(2)
C(24)	0.5160(8)	−0.0501(6)	0.1304(5)	0.071(3)
C(25)	0.3815(9)	−0.1237(7)	0.0718(5)	0.086(3)
C(26)	0.2712(10)	−0.2200(7)	0.0942(7)	0.095(4)
C(27)	0.2893(10)	−0.2443(7)	0.1713(8)	0.098(4)
C(28)	0.4208(8)	−0.1711(6)	0.2303(6)	0.079(3)
Cl(1)	0.8111(6)	0.1456(3)	0.5334(3)	0.203(2)
Cl(2)	0.7092(6)	−0.1163(3)	0.4921(3)	0.199(2)
C(29)	0.745(2)	0.0169(11)	0.4625(7)	0.189(8)

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

mmol) in Et_2O (5 mL). After 1 h, the white solid that had precipitated was isolated by decantation, washed with pentane (3 × 5 mL), and dried *in vacuo*: yield 0.093 g (79%); ^{1}H NMR ($CDCl_3$) δ 7.52−7.21 (m, 14H, aryl), 7.00−6.84 (m, 4H, aryl), 3.37 (br m, 2H, CH_2), 2.47 (br m, 6H, NCH_3), 0.39 (d, 3H, $^3J_{H,P}$ = 2.8 Hz, PdCH_3). Anal. Calcd for $C_{29}H_{29}N_2OPPd$: C, 62.32; H, 5.23; N, 5.01. Found: C, 62.38; H, 5.23; N, 5.09.

Preparation of [Pd(Me)(OC$_6$H$_5$)(PCN)]·HOC$_6$H$_5$ (14). To a solution of [$Pd(Me)_2$(PCN)] (**1**) (0.182 g, 0.40 mmol) in Et_2O (15 mL) was added phenol (0.075 g, 0.80 mmol). After 10 min, the white precipitate that had formed was isolated by decantation, washed with pentane (2 × 10 mL), and dried *in vacuo*. The product can be crystallized by slow diffusion of pentane into a CH_2Cl_2 solution, affording plate-shaped colorless crystals suitable for X-ray diffraction: yield 0.152 g (62%); ^{1}H NMR (C_6D_6) δ 9.30 (br s, 1H, O*H*), 7.43−6.78 (m, 19H, aryl), 6.53 (t, 1H, $^3J_{H,H}$ = 7 Hz, *p*-H PdOPh), 2.84 (s, 4H, CH_2), 2.32 (s, 6H, NCH_3), 0.98 (d, 3H, $^3J_{H,P}$ = 3.1 Hz, PdCH_3); ^{13}C NMR ($CDCl_3$) δ 66.58 (d, $^2J_{C,P}$ = 11 Hz, *C*H_2), 48.42 (N*C*H_3), 2.89 (d, $^2J_{C,P}$ = 5 Hz, Pd*C*H_3). Anal. Calcd for $C_{34}H_{36}NO_2PPd$: C, 65.02; H, 5.78; N, 2.23. Found: C, 64.88; H, 5.73; N, 2.29.

Preparation of [Pd(Me)(SC$_6$H$_5$)(PCN)] (15). To a solution of [Pd(Me)(OCH(CF_3)$_2$)(PCN)] (**10**) (0.10 g, 0.20 mmol) in benzene (15 mL) was added benzenethioacetate (0.030 g, 0.20 mmol). After 2 h, the orange solution was evaporated to dryness *in vacuo* and the residue was washed with pentane (2 × 10 mL) to afford a red solid, which was dried *in vacuo*: yield 0.08 g (70%); ^{1}H NMR (CD_3COCD_3) δ 7.90−7.30 (m, 12H, aryl), 7.10−6.70 (m, 3H, aryl), 2.82−2.58 (m, 4H, CH_2CH_2), 2.60 (s, 6H, NCH_3), 0.30 (d, 3H, $^3J_{H,P}$ = 3 Hz, PdCH_3). Anal. Calcd for $C_{34}H_{36}NPPdS$: C, 56.62; H, 5.78; N, 2.87. Found: C, 57.09; H, 5.73; N, 3.11.

Table 6. Final Coordinates and Equivalent Isotropic Thermal Properties of the Non-Hydrogen Atoms for 14 (esd's in Parentheses)[a]

atom	*x*	*y*	*z*	U_{eq} (Å^2)[a]
Pd(1)	1.01685(2)	0.20659(2)	0.21564(2)	0.0343(1)
P(1)	0.87715(8)	0.28440(8)	0.08664(7)	0.0345(2)
O(1)	1.1554(2)	0.1299(2)	0.3354(2)	0.0406(8)
N(1)	0.8646(3)	0.1735(3)	0.3417(2)	0.0384(12)
C(1)	0.8970(4)	0.0406(4)	0.3824(3)	0.0479(12)
C(2)	0.8745(4)	0.2317(4)	0.4320(3)	0.0521(14)
C(3)	0.7291(4)	0.2224(4)	0.3082(3)	0.0430(12)
C(4)	0.7031(3)	0.1732(3)	0.2154(3)	0.0402(12)
C(5)	0.6164(4)	0.1051(4)	0.2332(4)	0.0526(14)
C(6)	0.5868(4)	0.0593(4)	0.1514(4)	0.0586(16)
C(7)	0.6436(5)	0.0815(4)	0.0482(4)	0.0576(16)
C(8)	0.7294(4)	0.1510(4)	0.0276(4)	0.0464(12)
C(9)	0.7595(3)	0.1981(3)	0.1096(3)	0.0380(12)
C(10)	0.9341(3)	0.2811(3)	−0.0545(3)	0.0374(12)
C(11)	1.0211(4)	0.1722(4)	−0.0741(3)	0.0494(12)
C(12)	1.0652(5)	0.1598(5)	−0.1793(4)	0.0597(16)
C(13)	1.0234(5)	0.2558(5)	−0.2650(4)	0.0641(16)
C(14)	0.9398(5)	0.3629(5)	−0.2465(4)	0.0634(16)
C(15)	0.8953(4)	0.3768(4)	−0.1404(3)	0.0503(12)
C(16)	0.7803(4)	0.4406(3)	0.0908(3)	0.0392(12)
C(17)	0.6664(4)	0.4969(4)	0.0360(4)	0.0513(14)
C(18)	0.5943(4)	0.6134(4)	0.0438(5)	0.0622(16)
C(19)	0.6320(5)	0.6747(4)	0.1095(4)	0.0612(16)
C(20)	0.7437(5)	0.6201(4)	0.1639(4)	0.0595(16)
C(21)	0.8189(5)	0.5038(4)	0.1544(3)	0.0506(14)
C(22)	1.1605(4)	0.2452(5)	0.1108(4)	0.0584(14)
C(23)	1.2474(3)	0.0260(3)	0.3339(3)	0.0366(12)
C(24)	1.2421(4)	−0.0580(4)	0.2738(3)	0.0488(12)
C(25)	1.3372(5)	−0.1686(4)	0.2796(4)	0.0572(16)
C(26)	1.4414(5)	−0.1991(4)	0.3433(4)	0.0594(16)
C(27)	1.4501(4)	−0.1179(4)	0.4029(4)	0.0521(16)
C(28)	1.3554(4)	−0.0069(4)	0.3985(3)	0.0444(12)
O(2)	0.1742(4)	0.2704(4)	0.4635(3)	0.0710(14)
C(29)	0.2560(4)	0.3377(4)	0.4232(4)	0.0528(14)
C(30)	0.2683(5)	0.4191(5)	0.4827(4)	0.0676(17)
C(31)	0.3497(6)	0.4907(5)	0.4432(6)	0.081(2)
C(32)	0.4193(5)	0.4825(5)	0.3465(6)	0.077(2)
C(33)	0.4070(5)	0.4021(5)	0.2881(5)	0.0652(17)
C(34)	0.3261(4)	0.3305(4)	0.3253(4)	0.0550(14)

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

Preparation of [Pd(Me)(C≡CPh)(PN)] (16). Phenylacetylene (1.0 mL, 9.2 mmol) was added to a solution of [Pd(Me)(OCH(CF_3)$_2$)(PN)] (**2**) (0.24 g, 0.44 mmol) in diethyl ether (15 mL). After 15 min, the white precipitate that had formed was isolated, washed with pentane (2 × 10 mL), and dried *in vacuo*: yield 0.18 g (86%); ^{1}H NMR (CD_3COCD_3) δ 7.82−7.42 (m, 10H, Ar*H*), 7.28 (d, 2H, $^3J_{H,H}$ = 7 Hz, *o*-Ar*H*), 7.17 (t, 2H, $^3J_{H,H}$ = 7 Hz, *m*-Ar*H*), 7.06 (t, 1H, $^3J_{H,H}$ = 7 Hz, *p*-Ar*H*), 2.81 (s, 6H, NCH_3), 2.70−2.45 (m, 4H, CH_2CH_2), 0.51 (d, 3H, $^3J_{H,P}$ = 7.2 Hz, PdCH_3). Anal. Calcd for $C_{25}H_{28}NPPd$: C, 62.57; H, 5.88; N, 2.92. Found: C, 62.55; H, 5.95; N, 2.99.

Preparation of [Pd(Me)(C≡CPh)(tmeda)] (17). Phenylacetylene (0.25 mL, 2.3 mmol) was added to a solution of [Pd(Me)(OCH(CF_3)$_2$)(tmeda)] (0.85 g, 2.1 mmol) in Et_2O (10 mL) at 0 °C. After 15 min a white precipitate formed, and this was isolated by decantation, washed with pentane (2 × 5 mL), and dried *in vacuo*: yield 0.52 g (74%); ^{1}H NMR ($CDCl_3$, 273 K) δ 7.38 (d, 1H, $^3J_{H,H}$ = 7 Hz, *o*-Ph), 7.15 (m, 2H, *p*-Ph), 7.07 (m, 1H, *m*-Ph), 2.71−2.45 (m, 4H, CH_2CH_2), 2.66 (s, 6H, NCH_3), 2.49 (s, 6H, NCH_3), 0.31 (s, 3H, PdCH_3); ^{13}C NMR ($CDCl_3$, 273 K) δ 131.45 (Ar*C*), 128.40 (C_{ipso} Ar), 127.74 (Ar*C*), 124.78 (Ar*C*), 105.83 (C≡C), 103.64 (C≡C), 61.50 (*C*H_2), 58.78 (*C*H_2), 49.32 (N*C*H_3), 48.78 (N*C*H_3), −9.33 (Pd*C*H_3). Anal. Calcd for $C_{15}H_{24}N_2Pd$: C, 53.18; H, 7.14; N, 8.27. Found: C, 51.30; H, 6.85; N, 8.13.

Thermolysis of Alkynyl Complexes 16 and 17. A solution of **16** or **17** in acetone was heated at 50 °C for 2 h, and the solution was filtered through Celite to remove Pd(0). GLC analysis of the filtrate (diphenylmethane as internal standard) showed the formation of methylphenylacetylene. In

a similar experiment, CO was bubbled for 10 min through a solution of **16** and **17** followed by removal of Pd(0) by filtration. GLC analysis of the filtrate (diphenylmethane as internal standard) showed the formation of methylphenylacetylene and MeCOC≡CPh.

Reaction of 2 and $HOCH(CF_3)_2$ [*in Situ* Preparation of the Adduct $[Pd(Me)(OCH(CF_3)_2)(PN)]\cdot HOCH(CF_3)_2$ (18)]. A solution of **2** in toluene-d_8 (0.50 mL) was transferred to an NMR tube containing 1 equiv of $HOCH(CF_3)_2$. ^1H NMR showed the quantitative formation of the alcohol adduct **18**. Attempts to isolate this O−H···O hydrogen-bonded adduct by crystallization in toluene/pentane at −20 °C failed and the starting materials were recovered.

X-ray Structure Determination of 12 and 14. Crystals of **12** (yellow) and **14** (colorless) suitable for X-ray diffraction were glued to the tip of a Lindemann glass capillary and transferred to an Enraf-Nonius CAD4-F diffractometer. Accurate unit cell parameters and an orientation matrix were determined by least-squares refinement of the setting angles of 25 well-centered reflections (SET4)[23] in the ranges $12.4° < \theta < 19.3°$ and $16.5° < \theta < 24.7°$ for **12** and **14**, respectively. The unit cell parameters were checked for the presence of higher lattice symmetry.[24] Crystal data and details on data collection and refinement are presented in Table 4. Data were correlated for Lp effects and for the observed linear decay of the reference reflections. An empirical absorption extinction correction was applied (DIFABS)[25] for both complexes. The structures were solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92).[26] Both complexes were refined on F^2 by full-matrix least-squares techniques (SHELXL-93);[27] no observance criterion was applied during refinement. Thirty-one deviating reflections displaying an unequal background were omitted during the final refinements of complex **14**. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms, except for phenolic hydroxyl hydrogen (compound **14**), which was located on a difference Fourier map and subsequently included in the refinement. The methyl groups of both complexes were refined as rigid groups, allowing for rotation around the N−C bonds. 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 thermal parameter of their carrier atoms by a factor amounting to 1.5 for the hydroxyl and methyl hydrogen atoms and 1.2 for the other hydrogen atoms. Final positional parameters are listed in Tables 5 and 6 for **12** and **14**, respectively. Neutral atom scattering factors and anomalous dispersion corrections were taken from the *International Tables for Crystallography*.[28] Geometrical calculations and illustrations were preformed with PLATON;[29] all calculations were performed on a DECstation 5000 cluster.

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Supporting Information Available: Further details of the structure determinations, including atomic coordinates, bond lengths and angles, and thermal parameters for **12** and **14** (16 pages). Ordering information is given on any current masthead page.

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