Chemistry of Diamino-Ligated Methylpalladium(II) Alkoxide Complexes: Syntheses, X-ray Crystal Structures, and Hydrogen-Bond Formation

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Abstract: The reaction of diamino-ligated dimethylpalladium(II) complexes $[Pd(Me)_2(N\sim N)]$ (N∼N = tmeda, bpy) with an equimolar amount of 1,1,1,3,3,3-hexafluoro-2-propanol or (substituted) phenols affords the new complexes $[Pd(Me)(OR)(N\sim N)]$ (N∼N = tmeda, R = $CH(CF_3)_2$ (**1**), C_6H_5 (**3**), C_6H_4-4-NO_2 (**4**), C_6H_4-2-OH (**11**)); N∼N = bpy, R = $CH(CF_3)_2$ (**2**)). These methylpalladium(II) alkoxides and aryloxides are isolated in high yields as yellow-orange solids and are remarkably thermally stable. Mono- or bidentate ligands can substitute the tmeda ligand in **1** to afford a variety of methylpalladium alkoxide complexes $[Pd(Me)(OCH(CF_3)_2)L_2]$ (L_2 = bpy (**2**), $Ph_2PCH_2CH_2NMe_2$ (**12**), dppe (**13**), $2PMe_3$ (**14**)). Crystals of **1**, **3**, and **4** have been subjected to X-ray diffraction studies. Crystals of **1** are monoclinic, space group $P2_1/c$, with unit-cell dimensions a = 8.2054(5) Å, b = 17.2310(9) Å, c = 11.1191(12) Å, β = 105.701(7)°, and Z = 4. Crystals of **3** are orthorhombic, space group *Pbca*, with unit-cell dimensions a = 10.572(2) Å, b = 16.446(2) Å, c = 17.029(3) Å, and Z = 8. Crystals of **4** are orthorhombic, space group *Pbca*, with unit-cell dimensions a = 11.918(5) Å, b = 12.089(3) Å, c = 22.684(7) Å, and Z = 8. The molecular structures of these complexes show them to be square-planar species, and in **1** the C_β−H unit of the fluorinated alkoxide is directed toward the palladium center (H···Pd = 2.89(3) Å), in what can be interpreted as the incipient stage of a β-hydrogen elimination. The palladium alkoxide or aryloxide complexes **1**−**4** when treated with 1 equiv of the corresponding alcohol or (substituted) phenol afford O−H···O hydrogen-bonded adducts $[Pd(Me)(OR)(N\sim N)]\cdot HOR$ (N∼N = tmeda, R = $CH(CF_3)_2$ (**5**), C_6H_5 (**7**), C_6H_4-4-NO_2 (**8**); N∼N = bpy, R = $CH(CF_3)_2$ (**6**), C_6H_5 (**9**)). The X-ray molecular structures of $[Pd(Me)(OC_6H_5)(tmeda)]\cdot HOC_6H_5$ (**7**) and $[Pd(Me)(OC_6H_4\text{-}4\text{-}NO_2)(tmeda)]\cdot HOC_6H_4$-4-$NO_2$ (**8**) reveal that the aromatic alcohol is associated with the oxygen atom of the aryloxide through O−H···O hydrogen bonding. Crystals of **7** are monoclinic, space group $P2_1/c$, with unit-cell dimensions a = 15.5556(13) Å, b = 11.0416(10) Å, c = 12.0211(11) Å, β = 91.343(8)°, and Z = 4. Crystals of **8** are monoclinic, space group $P2_1/c$, with unit-cell dimensions a = 8.7029(5) Å, b = 15.6384(11) Å, c = 16.5188(9) Å, β = 90.096(5)°, and Z = 4. Comparison of the solid state structures of $[Pd(Me)(OC_6H_4\text{-}4\text{-}NO_2)(tmeda)]$ (**4**) and its HOC_6H_4-4-NO_2 adduct (**8**) reveal that an electron-withdrawing substituent on the aryloxide ring leads to geometric changes in the Pd−O−C unit. Proton NMR for **5**−**9** and the X-ray structural data of **7** and **8** indicate that the O−H···O hydrogen bonding in these adducts is strong both in solution and in the solid state. The thermodynamic parameters for the alkoxide−alcohol exchange in the adduct $[Pd(Me)(OCH(CF_3)_2)(tmeda)]\cdot HOCH(CF_3)_2$ (**5**) have been determined with NMR spin saturation transfer techniques and provide evidence for a five-coordinate species being the key intermediate in this intramolecular exchange reaction. Furthermore, the thermodynamic parameters for adduct formation, obtained by the Scatchard method, quantify the O−H···O hydrogen bond as being strong.

Introduction

Recently, the chemistry of late transition metal alkoxide complexes has attracted much attention.[1−9] One reason for this is that such complexes have been postulated as key intermediates in various transition metal-catalyzed processes.[2] Recent examples of (alkoxo)palladium-catalyzed processes include not only the perfectly alternating copolymerization of CO and olefins to produce polyketones,[3] but also the methoxycarbonylation of propyne to give methyl methacrylate.[4] An earlier belief that the metal-to-oxygen bond is weak, as a result of the occurrence of antibonding π-interactions between filled metal

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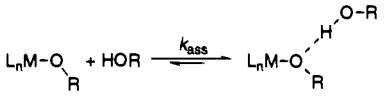
d-orbitals and oxygen lone pairs,[5] may have limited research in this area, and reports concerning late transition metal alkoxides and aryloxides are still rare, in particular when the other ligands are mono- or bidentate tertiary amines. It is now recognized, however, that the metal-to-oxygen bond may be of comparable strength or even stronger than the metal-to-carbon-(sp^3) bond.[6]

Reported interesting properties of late transition metal alkoxides include C−O bond formation,[7] insertion of small molecules into the metal-to-oxygen bond,[8] and β-hydrogen elimination from the alkoxide ligand to release aldehydes or ketones.[9] Another intriguing feature of late transition metal alkoxides is their ability to associate with alcohols, and so form adducts, through O−H···O hydrogen bonding (eq 1).[10]



(1)

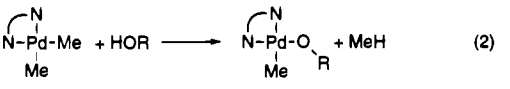
The nature of the O−H···O hydrogen bond has been studied in great detail in organic chemistry.[11] Now, studies of organometallic and inorganic complexes are showing that O−H···O hydrogen bonding can be an important factor in this field of chemistry as well.[12] In transition metal alkoxide chemistry the isolation of alcohol adducts shows the existence of a strong tendency for the formation of O−H···O hydrogen bonds.[10] Extreme examples of this tendency are reactions in which an additional amount of alcohol (accounting for O−H···O hydrogen bonding) is actually needed to drive the metal alkoxide formation to completion.[10e,h]

When the organic group R of an alcohol, ROH, is an electron-withdrawing unit, the assocation equilibrium (eq 1) is shifted to the right (adduct formation) as a result of the formation of a stronger O−H···O hydrogen bond. We have shown that the presence of a strong *trans*-positioned σ-donor is not a prerequisite for the formation of strong O−H···O hydrogen bonding (in terms of $\Delta H°$) and that the strength of the O−H···O hydrogen bond for transition metal alkoxides is determined by other factors as well.[13] Because the O−H···O hydrogen bond in transition metal alkoxide chemistry also persists to a large extent in solution,[10,13] detailed thermodynamic studies of this interaction using NMR spectroscopy[10a,13] or calorimetry[10b,13] are possible and have shown that this type of O−H···O hydrogen bond is fairly strong.

In the course of our study of N-ligated (aryloxo)palladium-(II) complexes of the type $[Pd(OR)_2L_2]$,[14] we have also observed O−H···O hydrogen-bond formation with aryl alcohols. The molecular structure of the "mixed" alkoxo(aryloxo)palladium-(II) adduct $[Pd(OCH(CF_3)_2)(OC_6H_5)(bpy)]\cdot HOC_6H_5$ shows the presence not only of an intermolecular O−H···O hydrogen bond but also of an intramolecular C−H···O interaction.[14a] We report here full details of our study on the synthesis, characterization, and properties of N-ligated methylpalladium(II) alkoxides or aryloxides of the type [Pd(Me)(OR)(N∼N)] and the adducts they form with alcohols. Thermodynamic data have been determined for the O−H···O bond interaction in the latter complexes, and the role and importance of this interaction are discussed.

Results and Discussion

Preparation of Methylpalladium Alkoxide and Aryloxide Species and Their Adducts. The 1:1 molar reaction of dimethylpalladium(II) complexes containing bidentate nitrogen donor ligands, *i.e.*, $[Pd(Me)_2(N\sim N)]$ (N∼N = tmeda, bpy), with organic compounds ROH has been used to prepare the new methylpalladium(II) alkoxide and aryloxide complexes [Pd(Me)-(OR)(N∼N)] (**1**−**4**) as shown in eq 2. This reaction, in which



(2)

1: R = $CH(CF_3)_2$, N∼N = tmeda
2: R = $CH(CF_3)_2$, N∼N = bpy
3: R = C_6H_5, N∼N = tmeda
4: R = C_6H_4-4-NO_2, N∼N = tmeda

CH_4 is the byproduct, has proved successful for 1,1,1,3,3,3-hexafluoro-2-propanol (pK_a = 9.3) and the phenols C_6H_5OH (pK_a = 9.9) and HOC_6H_4-4-NO_2 (pK_a = 7.3). Complexes **1**−**4** are obtained in moderate to good yield and are isolated as thermally stable, yellow-orange crystalline solids. In solution the 1,1,1,3,3,3-hexafluoro-2-propoxide complexes **1** and **2** decompose slowly with formation of Pd^0, whereas the aryloxide complexes **3** and **4** are stable in solution for several months. The decomposition of complexes **1** and **2** probably occurs by β-hydrogen elimination with formation of an intermediate methyl hydride complex, [Pd(H)(Me)(N∼N)], which undergoes reductive elimination of CH_4; related P-ligated alkylpalladium-(II) alkoxides are believed to decompose in a similar way.[9]

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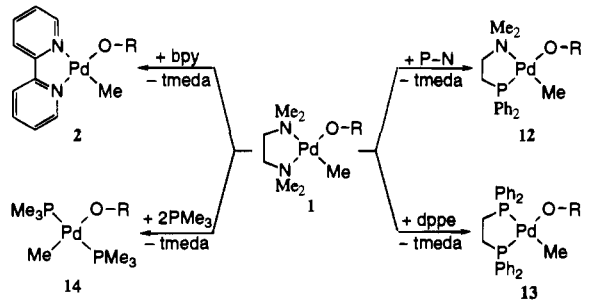
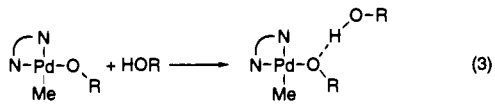


Figure 1. Ligand substitution reactions for methylpalladium alkoxide complex **1** (R = $CH(CF_3)_2$) with various donor ligands.

β-Hydrogen elimination of metal alkoxides is a classical method for the preparation of metal hydrides.[15]

The isolated methylpalladium alkoxide or aryloxide complexes **1**–**4**, when redissolved, react with 1 equiv of ROH (R = $CH(CF_3)_2$, C_6H_5, C_6H_4-4-NO_2) to give complexes formulated as [Pd(Me)(OR)(N~N)]·HOR (**5**–**8**) as shown in eq 3. These

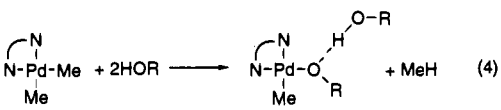


(3)

5: R = $CH(CF_3)_2$, N~N = tmeda
6: R = $CH(CF_3)_2$, N~N = bpy
7: R = C_6H_5, N~N = tmeda
8: R = C_6H_4-4-NO_2, N~N = tmeda

alcohol-associated adducts **5**–**8** can be isolated, in moderate to good yield, as thermally stable, yellow-orange crystalline solids. The alcohol or phenol free complexes **1**–**4** cannot be regenerated from the adducts **5**–**8** by different workup procedures (see Experimental Section), and this illustrates the stability of the O–H···O hydrogen bond in the latter species. The HOCH-$(CF_3)_2$ adducts **5** and **6** are stable in solution and are more thermally robust than the parent complexes **1** and **2**; *i.e.*, the O–H···O hydrogen bond appears to have a positive stabilizing effect. By means of X-ray crystallography and NMR spectroscopy (*vide infra*) it has indeed proved possible to unambiguously establish that the adducts **5**–**8** have strong O–H···O hydrogen bonding both in the solid state and in solution.

The O–H···O hydrogen-bonded adducts **5**–**8** can also be prepared directly by the addition of 2 equiv of alcohol or (substituted) phenol to the corresponding N-ligated dimethylpalladium(II) complexes (eq 4). This route has also been used



(4)

5: R = $CH(CF_3)_2$, N~N = tmeda
6: R = $CH(CF_3)_2$, N~N = bpy
7: R = C_6H_5, N~N = tmeda
8: R = C_6H_4-4-NO_2, N~N = tmeda
9: R = C_6H_5, N~N = bpy
10: R = C_6H_3-2,4-Me_2, N~N = tmeda

to prepare the new adducts [Pd(Me)(OC_6H_5)(bpy)]·HOC_6H_5 (**9**) and [Pd(Me)(OC_6H_3-2,4-Me_2)(bpy)]·HOC_6H_3-2,4-Me_2 (**10**). The synthesis of these latter adducts is interesting in that the addition of 1 equiv of phenol or 2,4-dimethylphenol to [$Pd(Me)_2$(bpy)] does not produce the expected aryloxide complex but 1/2 equiv of the adduct (**9** or **10**) with 1/2 equiv of unreacted starting material. It appears, therefore, that an additional amount of aryl alcohol is needed (accounting for O–H···O hydrogen bonding) in order to drive the palladium aryloxide formation to completion.

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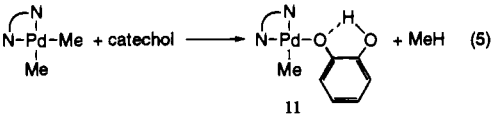
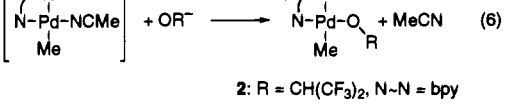
The reaction of an equimolar amount of catechol with [Pd-$(Me)_2$(tmeda)] produces [Pd(Me)(OC_6H_4-2-OH)(tmeda)] (**11**) which contains, in addition to the Pd–O bond, an intramolecular O–H···O hydrogen bond with the *o*-OH group (eq 5). This complex shows properties (*vide infra*) like those found for the alcohol adducts **5**–**10** containing intermolecular O–H···O hydrogen bonds.



(5)

The palladium alkoxide complex [Pd(Me)($OCH(CF_3)_2$)-(tmeda)] (**1**) is a useful starting material for the preparation of a variety of methylpalladium(II) fluorinated alkoxide complexes (see Figure 1). In benzene solution the tmeda ligand of **1** is smoothly substituted by bpy, (diphenylphosphino)-*N*,*N*′-dimethylethylenediamine (P~N), or 1,2-bis(diphenylphosphino)-ethane (dppe) to produce the fluorinated alkoxide complexes [Pd(Me)($OCH(CF_3)_2$)(bpy)] (**2**), [Pd(Me)($OCH(CF_3)_2$)(P~N)][16] (**12**), and [Pd(Me)($OCH(CF_3)_2$)(dppe)] (**13**), respectively. Reaction of **1** with PMe_3 results in the formation of the *trans* complex [Pd(Me)($OCH(CF_3)_2$)(PMe_3)$_2$] (**14**). Complexes **13** and **14** have been described before and were identified by comparison of their ^1H and ^{31}P NMR spectra with the literature data.[10a] This displacement of tmeda in **1** by other ligands confirms the excellent applicability of tmeda-ligated palladium complexes as versatile starting materials for the preparation of a large variety of palladium(II) complexes.[17] Surprisingly, the attempted substitution of the tmeda ligand in the aryloxide complex [Pd(Me)(OC_6H_5)(tmeda)] (**3**) for other ligands failed and the starting materials were recovered.

An alternative route for the preparation of the fluorinated alkoxide complex [Pd(Me)($OCH(CF_3)_2$)(bpy)] (**2**) involves the reaction of a palladium complex cation, [Pd(Me)(MeCN)-(bpy)]$^+$, with $NaOCH(CF_3)_2$ (eq 6). A conceptually similar



(6)

2: R = $CH(CF_3)_2$, N~N = bpy

reaction of an acetone-solvated platinum cation with KOH was employed by Bennett *et al.* to prepare interesting methyl-(hydroxo)platinum(II) complexes.[18] An important advantage of the "palladium complex cation" route depicted in eq 6 is that methylpalladium(II) alkoxide complexes are generated without any risk of contamination by the corresponding alcohol adduct. The routes described in eqs 2–5, using dimethylpalladium(II) complexes as starting materials all require use of exactly equimolar amounts of the alcohol as even a small excess immediately leads to the formation of O–H···O hydrogen-bonded species. Unfortunately, this palladium complex cation route has so far only been successfully applied for the synthesis of 2,2′-bipyridine-coordinated methylpalladium(II) alkoxide complexes; when the bidentate N-ligand tmeda is used, this method leads to the formation of palladium metal and unidentified organic products.

(16) An alternative synthesis of **12** comprises the reaction of HOCH-$(CF_3)_2$ with [$Pd(Me)_2$(P~N)]: Kapteijn, G. M.; Spee, M. P. R.; Spek, A. L.; Grove, D. M.; van Koten, G. Unpublished results.

(17) (a) de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907. (b) de Graaf, W.; Boersma, J.; van Koten, G. *Organometallics* **1990**, *9*, 1479. (c) Markies, B. A.; Rietveld, M. H. P.; Boersma, J.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **1992**, *424*, C12.

(18) (a) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738. (b) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, 119.

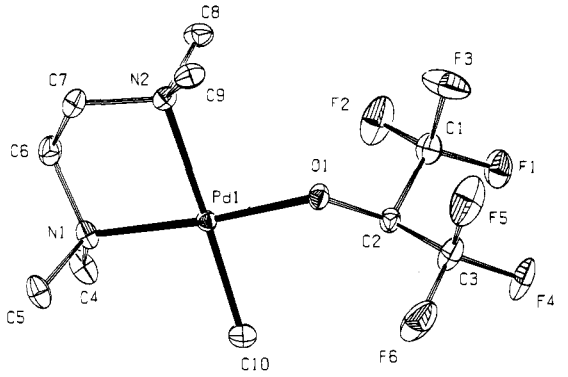


Figure 2. ORTEP (30% probability level) drawing of **1**.

Molecular Structures of Methylpalladium Alkoxide or Aryloxide Complexes 1, 3, and 4 and the O−H···O Hydrogen-Bonded Adducts 7 and 8. Figure 2 shows the molecular structure of the fluorinated alkoxide complex [Pd(Me)(OCH-$(CF_3)_2$)(tmeda)] (**1**), and Figure 3 shows the molecular structures of the aryloxide complexes [Pd(Me)(OC_6H_4-4-NO_2)(tmeda)] (**4**) and [Pd(Me)(OC_6H_4-4-NO_2)(tmeda)]·HOC_6H_4-4-NO_2 (**8**), respectively. Selected bond lengths and angles for the complexes **1**, **3**, **4**, **7**, and **8** are summarized in Table 1.

All five complexes possess an approximate square-planar coordination geometry with adjacent, interligand angles around the palladium centers falling in the range 84.6(2)−91.7(1)°. A special feature of complex **1** is that the proton of the OCH-$(CF_3)_2$ moiety is oriented toward the middle of the Pd−CH_3 bond and the distance of this proton from palladium (d(Pd···H) = 2.89(2) Å) is slightly smaller than the sum of the van der Waals radii. This separation may be regarded as the incipient stage of a β-hydrogen elimination, involving transfer of the proton from the $OCH(CF_3)_2$ moiety to the metal center that would afford a palladium hydride and hexafluoroacetone. The molecular structure of **1** also reveals the presence of a possible electrostatic C−H···O interaction from a NMe group with the oxygen of the $OCH(CF_3)_2$ unit (d[C(9)−H(9)···O(1)] = 3.106-(4) Å). This type of interaction may be termed a steering interaction which, although small in energy (1−2 kcal mol^{-1}), is sufficient to select a preferred molecular conformation.[19] We have reported earlier another example of a C−H···O interaction in a mixed alkoxo(aryloxo)palladium(II) complex.[14a]

Complexes **7** and **8** show the association of phenol or p-nitrophenol, respectively, to the aryloxide ligand through O−H···O hydrogen bonding (d(O···O) = 2.575(3) and 2.631-(4) Å, respectively). Hydrogen bonds are referred to as strong when the O···O distance is in the range 2.50−2.65 Å,[11e] and on this basis we conclude that the O−H···O interaction in **7** and **8** is reasonably strong. The distance between the two oxygen atoms of **7** and **8** is comparable to O···O distances both in organic molecules displaying hydrogen bonding[11] and in some other late transition metal alkoxide adducts (see Table 2). The Pd−O distances in the nonassociated complexes **1**, **3**, and **4** (2.020(2), 2.024(3), and 2.029(4) Å, respectively) fall within the range of Pd−O distances found in related palladium alkoxide and aryloxide complexes (see Table 2). The phenol and p-nitrophenol adducts **7** and **8** show Pd−O distances of 2.037-(2) and 2.043(2) Å, respectively; *i.e.*, association of an alcohol causes a small lengthening of the Pd−O bond by ~0.013 Å. A similar elongation of the Pd−O bond upon adduct formation has been reported by Kim *et al.* for *trans*-[Pd(Me)(OC_6H_5)-(PMe_3)$_2$] with phenol.[10a] Another geometrical parameter which is sensitive to O−H···O bond formation is the C−O bond length of the aryloxide ligand. In the adducts **7** and **8** this bond is longer by 0.022 and 0.034 Å, respectively, than the corresponding bond in the alcohol free complexes **3** and **4**. The presence of a NO_2 substituent on the aromatic ring also influences the C−O bond length (d(C−O) values for **3** and **4** are 1.314(6) and 1.286(6) Å, respectively) as a result of resonance and inductive effects. In all tmeda complexes **1**, **3**, **4**, **7**, and **8** studied here the Pd−N(2) bond *trans* to the methyl group (range: 2.178(3)−2.194(2) Å) is considerably longer than the Pd−N(1) bond *cis* to the methyl group (range: 2.060(5)−2.080-(2) Å), reflecting the larger *trans* influence of the methyl ligand as compared with the alkoxide (or phenoxide) ligands.

Association of Alcohol with Methylpalladium Alkoxide or Phenoxide Complexes. IR spectra of the hydrogen-bonded complexes **5**−**10** in KBr disks show a broad peak at 2350−2750 cm^{-1}. This absorption corresponds to ν(O−H) vibration of the hydrogen-bonded OH group in the aryl or fluorinated alcohol, and its value is indicative of a medium to strong hydrogen bond.[11] In order to quantify the strength of these hydrogen bonds in solution we determined the equilibrium constants (K_{ass}) for the association of 1,1,1,3,3,3-hexafluoro-2-propanol or phenol with methylpalladium complexes [Pd(Me)-(OCH$(CF_3)_2$)(tmeda)] (**1**) or [Pd(Me)(OC_6H_5)(tmeda)] (**3**) (see eq 1) with application of the Scatchard equation to ^{1}H NMR data obtained at various temperatures.[22] This method is based on the change of the chemical shift of the OH resonance (at a fixed concentration of hydrogen-bond donor) with variation of the concentration of the hydrogen-bond acceptor (*i.e.*, palladium alkoxide or phenoxide). An important condition made in the derivation of the Scatchard equation is that the ratio of the concentration of palladium alkoxide (or phenoxide) complex to that of alcohol (or phenol) is high (typically >15:1). This condition in combination with the low boiling point of $CDCl_3$ makes it difficult in practice to achieve a wide range of saturation factors. The ^{1}H NMR spectra of mixtures of 1,1,1,3,3,3-hexafluoro-2-propanol (fixed at 0.012 M) and **1** ([complex]/[alcohol] ranges from 15 to 35) or phenol (fixed at 0.010 M) and **3** ([complex]/[phenol] ranges from 18 to 40) in $CDCl_3$ show the O−H resonance in the range 9.7−7.9 ppm. This OH resonance shifts to higher field upon raising the temperature or on decreasing the concentration of palladium alkoxide (or phenoxide). Thermodynamic parameters for the association have been derived from the temperature dependence of the equilibrium constant (K_{ass}) through use of a van't Hoff plot in which ln K_{ass} is plotted against $1/T$. The resulting plots for the association of 1,1,1,3,3,3-hexafluoro-2-propanol to **1** and phenol to **3** are shown in Figure 4. The thermodynamic parameters obtained from Figure 4 for association of 1,1,1,3,3,3-hexafluoro-2-propanol to **1** (at 298 K) are $\Delta H° = -34.7 \pm 2.6$ kJ mol^{-1}, $\Delta S° = 83.6 \pm 8.1$ J K^{-1} mol^{-1}, and $K_{ass} = 53$ L mol^{-1} ($\Delta G° = -9.9 \pm 3.6$ kJ mol^{-1}), whereas values for phenol association to **3** (at 298 K) are $\Delta H° = -29.1 \pm 2.4$ kJ mol^{-1}, $\Delta S° = 58.6 \pm 7.4$ J K^{-1} mol^{-1}, and $K_{ass} = 105$ L mol^{-1} ($\Delta G° = -11.6 \pm 3.3$ kJ mol^{-1}). The unequality affinity for O−H···O bond formation in **1** and **3** as expressed in the K_{ass} values can be seen to derive from very different $\Delta S°$ values. The enthalpy data indicate that the hydrogen bonds observed for **1** and **3** are both strong when compared to the intermolecular O−H···O hydrogen bonding of aliphatic alcohols ($\Delta H° = -12$ to -25 kJ mol^{-1}).[11] An overview of thermodynamic parameters

(19) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290.
(20) Structures of palladium bis(alkoxides) based on diethanolamines ($RN(CH_2CH_2OH)_2$) show the formation of either intra- or intermolecular O−H···O hydrogen bonds to depend on the R substituent (R = Me, inter; R = CH_2CH_2OH, intra): Kapteijn, G. M.; Grove, D. M.; van Koten, G. Unpublished results.
(21) (a) Simpson, R. D.; Bergman, R. G. *Organometallics* **1993**, *12*, 781. (b) Osakada, K.; Takizawa, T.; Tanaka, M.; Yamamoto, T. *J. Organomet. Chem.* **1994**, *473*, 359.
(22) See ref 11b, p 173.

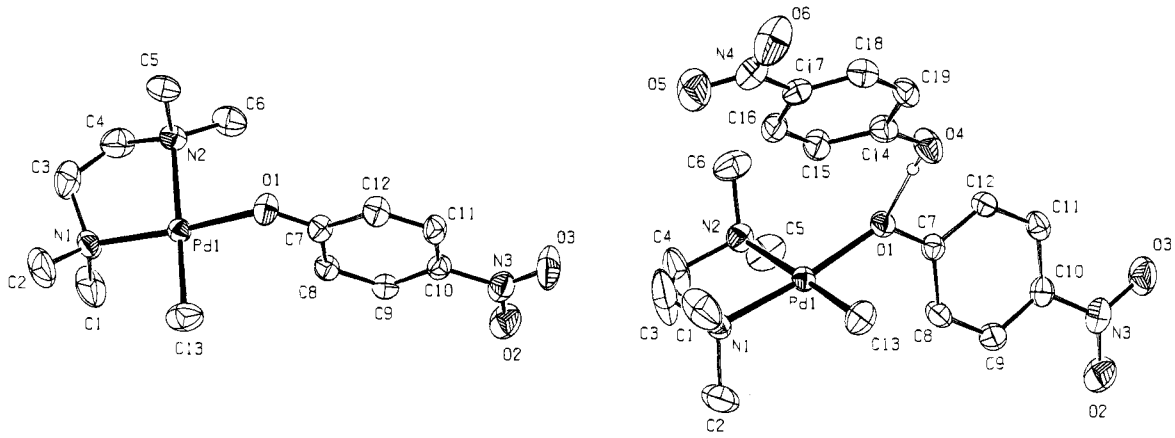


Figure 3. ORTEP (30% probability level) drawings of **4** (left) and **8** (right).

Table 1. Selected Bond Distances (Å), Bond Angles (deg), and Dihedral Angles (deg) for the Complexes [Pd(Me)(OR)(tmeda)] (**1**, **3**, and **4**) and their Adducts [Pd(Me)(OR)(tmeda)]·HOR (**7** and **8**)[a]

	1 (R = $CH(CF_3)_2$)	**3** (R = C_6H_5)	**7** (R = C_6H_5)	**4** (R = C_6H_4-4-NO_2)	**8** (R = C_6H_4-4-NO_2)
			Bond Distances		
Pd–O	2.020(2)	2.024(3)	2.037(2)	2.029(4)	2.043(2)
Pd–C	2.017(3)	2.010(5)	2.025(3)	1.997(7)	2.012(4)
Pd–N(1)	2.080(2)	2.071(4)	2.071(2)	2.060(5)	2.072(3)
Pd–N(2)	2.183(2)	2.178(3)	2.194(2)	2.178(5)	2.181(3)
C–O[b]	1.365(3)	1.314(6)	1.336(4)	1.286(6)	1.320(4)
C–O[c]			1.349(3)		1.347(4)
O···O			2.575(3)		2.631(4)
			Bond Angles		
Pd–O–C	121.8(1)	122.8(3)	122.0(2)	125.5(3)	125.2(2)
C–Pd–O	91.71(9)	88.4(2)	89.4(1)	89.6(2)	89.4(1)
N–Pd–N	84.94(7)	84.6(2)	84.9(1)	85.6(2)	85.1(1)
O–H···O			167(2)		176(5)
			Dihedral Angles		
N–C–C–N	−56.7(3)	−54.1(7)	56.3(4)	−55.4(7)	34.7(9)
Pd–O–C–C		25.4(6)	−29.6(3)	0.8(7)	1.1(5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Alkoxide or aryloxide oxygen. [c] (Aryl) alcohol oxygen.

Table 2. Overview of Characteristic Bond Distances and Angles of Transition Metal Alkoxide or Aryloxide Adducts

entry	compound	*d*(O···O) (Å)	∠(O–H···O) (deg)	*d*(M–O) (Å)	ref
		Palladium(II) Alkoxides and Aryloxides			
1	[Pd(OPh)(C_6H_3{CH_2NMe_2}$_2$-2,6)]·HOPh	2.567(6)		2.139(4)	13
2	[Pd(Me)(OPh)(tmeda)]·HOPh	2.575(3)	167	2.037(2)	this work
3	*trans*-[Pd(H)(OC_6F_5)(PCy_3)$_2$]·HOC_6F_5	2.59(3)	164.7	2.181(2)	10e
4	*trans*-[Pd(Me)(OPh)(PMe_3)$_2$]·HOPh	2.593(4)	169.9	2.134(3)	10a
5	*trans*-[Pd(Me)(OPh)(PMe_3)$_2$]·HOCH(CF_3)(Ph)	2.601(4)	165.4	2.107(2)	10a
6	[Pd(Me)(OC_6H_4-NO_2)(tmeda)]·HOC_6H_4-NO_2	2.631(4)	176	2.043(2)	this work
7	*trans*-[Pd(OPh)$_2$(pyrrolidine)$_2$]·2HOPh	2.638(4)		2.018(2)	13
8	*trans*-[Pd(H)(OPh)(PCy_3)$_2$]·HOPh	2.64(4)	168.3	2.135(2)	10e
9	[Pd(OPh)(OCH(CF_3)$_2$)(bpy)]·HOPh[a]	2.642(8)		1.997(5)	14
10	[Pd(OCH_2CH_2N(Me)(CH_2CH_2OH))$_2$][b]	2.652(5)	177.0	2.002(3)	20
11	[Pd(OCH_2CH_2N(CH_2CH_2OH)$_2$)$_2$]	2.665(5)	167.0	2.006(3)	20
		Other Transition Metal Alkoxides and Aryloxides			
12	*fac*-[(CO)$_3$(depe)Re(OCH_2CH_3)]·HOC_6H_4-4-Me	2.532(5)	173.2	2.154(3)	21a
13	*trans*-[Ni(H)(OPh)(PBz_3)$_2$]·HOPh	2.544(6)		1.949(4)	10i
14	[Pt(OC_6H_4-2-OH)(C_6H_3{CH_2NMe_2}$_2$-2,6)][c]	2.57(2)	117.0	2.10(2)	16b
15	*trans*-[Ni(Me)(OPh)(PMe_3)$_2$]·HOPh	2.602(8)	165.6	1.932(5)	10a
16	[Rh(OC_6H_4-4-Me)(PMe_3)$_3$]·HOC_6H_4-4-Me	2.62(5)			10b
17	[Pt(Me)(OCH(CF_3)$_2$(PMe_3)$_2$]·HOCH(CF_3)$_2$	2.63(5)		2.07(3)	10k
18	[Ru($OCH_2C_6H_4$)(PMe_3)$_4$]·$HOCH_2C_6H_4$	2.75(2)[d]		2.144(8)	10j

[a] The oxygen coordinated to Pd is also taking part in a C–H···O hydrogen bond. [b] Intermolecular O–H···O hydrogen bonds result in a two-dimensional molecular network. [c] The unusually acute O–H···O angle is a result of an intramolecular O–H···O hydrogen bond. [d] This distance is probably a result of the high pK_a value for benzyl alcohol.

obtained using calorimetric titration or the Scatchard method for the association of alcohols with some late transition metal alkoxides or aryloxides is shown in Table 3. This table includes the enthalpy values of O–H···O hydrogen bond formation not only for late transition metal mono(alkoxide) complexes (entries 1–3 and 6–10) but also for late transition metal bis(aryloxide) complexes (entries 4 and 5). For several palladium and platinum complexes (entries 3–6 and 9–10 in Table 3) the $\Delta H°$ values are in the range −17 to −25 kJ mol^{-1} even though there is a large variety of C, O, and P donors present *trans* to the alkoxide ligand. This indicates that strong *trans*-positioned σ-donors are not a prerequisite for strong O–H···O hydrogen bonding and that the strength is determined by other factors as well.[13] The enthalpy values obtained by us for association of an alcohol

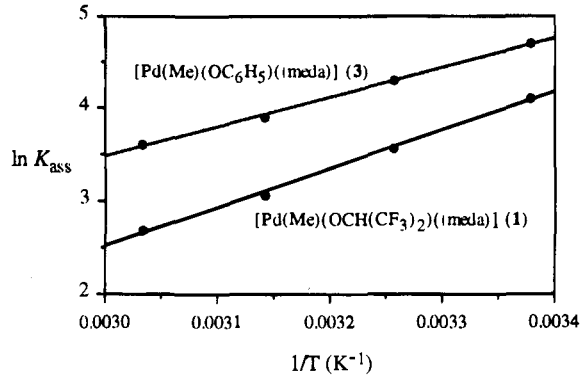


Figure 4. Van't Hoff plots for association of HOR to **1** and **3**.

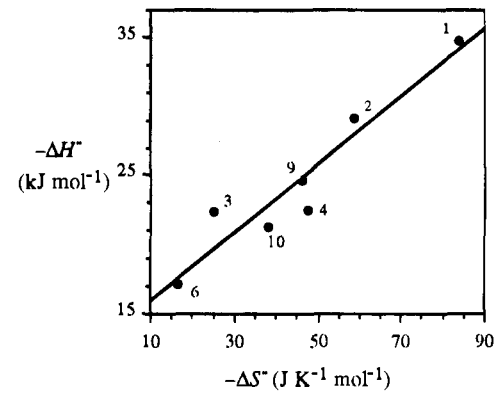


Figure 5. Plot of $-\Delta H°$ vs $-\Delta S°$ for alcohol O−H···O hydrogen bonds to late transition metal alkoxides. The entries are summarized in Table 3.

with both [Pd(Me)($OCH(CF_3)_2$)(tmeda)] (**1**) and [Pd(Me)(OC_6H_5)(tmeda)] (**3**) in $CDCl_3$ are substantially higher than those obtained for other palladium and platinum alkoxides. However, our values are lower than for association of HOC_6H_4-4-Me to the rhodium(I) aryloxide complex [Rh(OC_6H_4-4-Me)(PMe_3)$_2$] in benzene (entry 8) or cyclohexane (entry 7), and a possible explanation could lie in polarity differences between the solvents used in these two studies.[19,23] The $\Delta H°$ differences for O−H···O hydrogen-bond formation of diamine (tmeda) chelate complexes **1** and **3** with alcohol or phenol are significantly higher (~10 kJ mol^{-1}) than those reported for analogous phosphine-ligated palladium alkoxides and phenoxides (entry 3 and 6). We believe that in complexes **1** and **3** the purely σ-donating amine ligand tmeda increases the nucleophilicity of the metal center more than a phosphine does and this leads to a higher negative charge on the oxygen atom of the alkoxide or phenoxide unit and, consequently, to the formation of stronger O−H···O hydrogen bonds. The reason that the phenoxide complex **3** produces a smaller enthalpy value for O−H···O hydrogen bond formation than the alkoxide complex **1** is almost certainly due to distribution of the negative charge of the oxygen atom over the aromatic ring by resonance stabilization. It is known that charged delocalized anions, including phenoxide, form weaker hydrogen bonds than nondelocalized anions.[24] Thus, the strength of the O−H···O hydrogen bond in organometallic alkoxide or aryl oxide complexes is governed by two factors, firstly the σ-donor strength of the group in the *trans* position with respect to the OR unit (a stronger σ-donor affords a stronger O−H···O hydrogen bond) and secondly charge delocalization within the −OR fragment (reducing the strength of the O−H···O hydrogen bond).

Enthalpy versus Entropy in Adduct Formation. There is now a reliable set of thermodynamic parameters for alcohol association to late transition metal alkoxide complexes in chlorocarbon solvents (see Table 3), and as shown in Figure 5 these data provide a reasonable straight line correlation between $\Delta H°$ and $\Delta S°$ for formation of transition metal alkoxide adducts with $\Delta S° = 4.04\Delta H° + 54.4$ ($\Delta H°$ in kJ mol^{-1}, $r^2 = 0.90$).

In organic chemistry several authors have demonstrated that there is a monotonic relationship between $\Delta H°$ and $\Delta S°$ for O−H···O hydrogen-bond formation between alcohols and other organic compounds such as aldehydes, ketones, esters, amines, and amides ($r^2 = 0.69$−0.93).[11c] Shepp and Bauer have postulated that the observed linear relationships can be explained in the following way.[25] On formation of an intermolecular O−H···O hydrogen bond (eq 1) there will be a loss of entropy ($\Delta S°$) which can be regarded as being made up of two separate terms, ΔS_{trans} and $\Delta S_{internal}$ (eq 7). ΔS_{trans} is negative because

$$\Delta S° = \Delta S_{trans} + \Delta S_{internal} \quad (7)$$

of the loss of degrees of translational freedom which makes the major contribution to the observed entropy of the reaction. However, $\Delta S_{internal}$ should be positive because of the gain of new rotational and vibrational freedom as a consequence of the formation of a new (O−H···O) bond. On the one hand, if the new O−H···O hydrogen bond is strong, then the force constants describing the new internal vibrations will be large and the $\Delta S_{internal}$ associated with them will be relatively small, leading to a large overall negative $\Delta S°$. On the other hand, weak O−H···O hydrogen bonds will produce a large gain in $\Delta S_{internal}$, which cancels the ΔS_{trans}, producing a small overall negative $\Delta S°$. This postulate, which is valid for hydrogen bonds in organic molecules, now also seems correct for the formation of O−H···O hydrogen bonds in transition metal alkoxide chemistry.

The observed linear relationship between $\Delta H°$ and $\Delta S°$ which we find for the first time with late transition metal alkoxides allows us to make confident predictions regarding K_{ass} of such complexes with alcohols. For example, if we take O−H···O hydrogen bonds of phenol with a given $\Delta H°$ of −20 kJ mol^{-1}, these will produce expected $\Delta S°$ values varying from −56 J K^{-1} mol^{-1} with aldehydes[26] to −26 J K^{-1} mol^{-1} with late transition metal alkoxides. This means that the equilibrium constants (298 K) will differ markedly for these systems, all due to the entropy effect; the calculated equilibrium constants (K_{ass}) for phenol with aldehydes or late transition metal alkoxides are 3.8 and 140.5, respectively (all K_{ass} values expressed in L mol^{-1}). Thus, adduct formation of transition metal alkoxides with alcohols is controlled by the entropy term, and it is this term which also controls adduct formation for several organic systems.[11c]

Solution Behavior of Alcohol Adducts: Exchange of the Alkoxide Group between the Alkoxide Ligand and Hydrogen-Bonded Alcohol. The O−H···O hydrogen-bonded adducts **5**−**10** show two sets of ^{1}H NMR resonances corresponding to the alkoxide or (substituted) phenoxide unit (Pd−OR) and the associated alcohol or (substituted) phenol (ROH). This observation means that alkoxide−alcohol exchange is slow on the NMR time scale. However, phenoxide−phenol exchange is fast on the laboratory time scale; the 1:1 addition of perdeuteriophenol (C_6D_5OD) to a $CDCl_3$ solution of the phenoxide complex **3**

(23) Chloroform can form C−H···O bonds: Green, R. D. *Hydrogen Bonding in C-H Groups*; Macmillan: London, 1974.
(24) Meor-Ner, M.; Sieck, L. W. *J. Am. Chem. Soc.* **1986**, *108*, 7525.
(25) Shepp, B.; Bauer, K. *J. Am. Chem. Soc.* **1954**, *76*, 265.
(26) The relation obtained for O−H···O hydrogen bonding of phenol to aldehydes is $\Delta S° = 3.10\Delta H° + 6.0$ ($\Delta H°$ in kJ mol^{-1}; nine data points): Murthy, A. S. N.; Rao, C. N. R. *Appl. Spectrosc. Rev.* **1968**, *2*, 69.
(27) de Graaf, W.; Boersma, J.; Grove, D. M.; Spek, A. L.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 299.

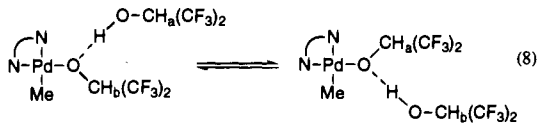
Table 3. Overview of Thermodynamic Parameters for Association of Alcohols with Late Transition Metal Alkoxide or Aryloxide Complexes[a]

entry	compound	R in HOR	solvent	$\Delta H°$ (kJ mol^{-1})	ref
	Palladium(II) Alkoxides and Aryloxides				
1	[Pd(Me)(OCH(CF$_3$)$_2$)(tmeda)], **1**	CH(CF$_3$)$_2$	$CDCl_3$	−34.7	this work
2	[Pd(Me)(OC$_6$H$_5$)(tmeda)], **3**	C$_6$H$_5$	$CDCl_3$	−29.1	this work
3	*trans*-[Pd(Me)(OC$_6$H$_5$)(PMe$_3$)$_2$]	C$_6$H$_5$	CD_2Cl_2	−23.5	10a
4	*trans*-[Pd(OC$_6$H$_5$)$_2$(pyrrolidine)$_2$]	C$_6$H$_5$	$CDCl_3$	−22.6	13
5	*trans*-[Pd(OC$_6$H$_5$)$_2$(pyrrolidine-Me)$_2$]	C$_6$H$_5$	$CDCl_3$	−22.2	13
6	[Pd(Me)(OC$_6$H$_5$)(dmpe)]	C$_6$H$_5$	CD_2Cl_2	−17.1	10a
	Other Transition Metal Alkoxides and Aryloxides				
7	[Rh(OC$_6$H$_4$-4-Me)(PMe$_3$)$_3$]	C$_6$H$_4$-4-Me	hexane	−58.6	10b
8	[Rh(OC$_6$H$_4$-4-Me)(PMe$_3$)$_3$]	C$_6$H$_4$-4-Me	benzene	−47.9	10b
9	*cis*-[Pt(Me)(OCH(CF$_3$)$_2$)(PMe$_3$)$_2$]	CH(CF$_3$)$_2$	toluene	−24.7	10f
10	*cis*-[Pt(Me)(OCH(CF$_3$)$_2$)(PMe$_3$)$_2$]	CH(CF$_3$)$_2$	CD_2Cl_2	−21.3	10f

[a] In the case of a deuterated solvent the Scatchard method was applied; calorimetry was used when nondeuterated solvents were used.

immediately results in the appearance of signals for (associated) phenol and reduction of the phenoxide ligand signals to half their original intensity.

The ^{1}H NMR spectra ($C_6D_5CD_3$) of the adduct **5** at 25 °C show well-resolved pairs of septet signals for the OC*H* hydrogens of the fluorinated alkoxide ligand and the associated fluorinated alcohol at 4.40 and 4.56 ppm, respectively. Raising the temperature (25−80 °C) causes a high-field shift of the septet at 4.56 ppm toward the position of unassociated alcohol; the other septet (from the alkoxide unit) remains at the same resonance position. Surprisingly, 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 the tmeda adduct **5**) that there is intramolecular alkoxide−alcohol exchange with OC*H* hydrogens of the alkoxide and alcohol coalescing at 0 °C.[10a] The same exchange process was proposed earlier in a study of rhodium(I) aryloxide complexes having associated phenol.[10b] In our system the alkoxide−alcohol exchange process is not observed directly due to a shift of the association equilibrium at higher temperatures toward unassociated palladium alkoxide complex and free alcohol (eq 1) as explained below. Therefore, in order to determine thermodynamic parameters for the intramolecular alkoxide−alcohol exchange for complex **5** (eq 8), spin saturation transfer (sst) experiments



(8)

using the Forsén−Hoffman method[28] were performed at low temperature. The rate constants (k) and lattice relaxation times for the alkoxide OC*H* hydrogen (T_b) and associated alcohol OC*H* hydrogen (T_a) were determined at four different temperatures in the range 254−298 K (see the Experimental Section). Changing the concentration of complex **5** does not influence the rate constant (k) for the exchange process, indicating that it indeed proceeds mainly by an intramolecular mechanism. On the basis of the Arrhenius equation the relationship between ln k and $1/T$ as derived from the ^{1}H NMR data provides the activation energy E_a = 60.8 ± 1.7 kJ mol^{-1} and the frequency factor $A = 7.1 \times 10^{10}$ s^{-1}. Figure 6 shows a plot of ln(k/T) versus $1/T$ that provides through use of the Eyring equation the following thermodynamic parameters for the exchange process: $\Delta G° = 70.1 \pm 2.6$ kJ mol^{-1}, $\Delta H° = 58.6 \pm 2.2$ kJ mol^{-1}, and $\Delta S° = -38.6 \pm 4.5$ J K^{-1} mol^{-1}. The Gibbs free energy for the intramolecular alkoxide−alcohol exchange in complex **5** is considerably higher than those reported for analogous phosphine-ligated palladium alkoxide complexes ($\Delta G° = 55-60$ kJ mol^{-1}).[10a]

(28) Mann, B. E. *J. Magn. Reson.* **1976**, *21*, 17 and references cited therein.

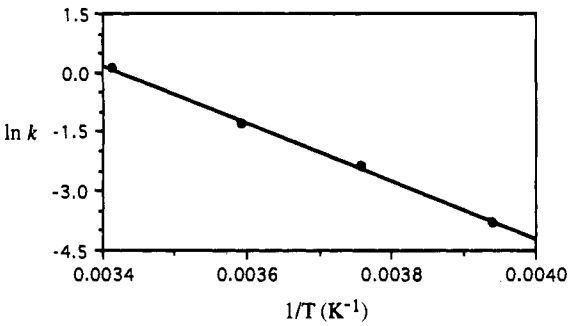


Figure 6. Eyring plot for the intramolecular alkoxide−alcohol exchange process in complex **5**.

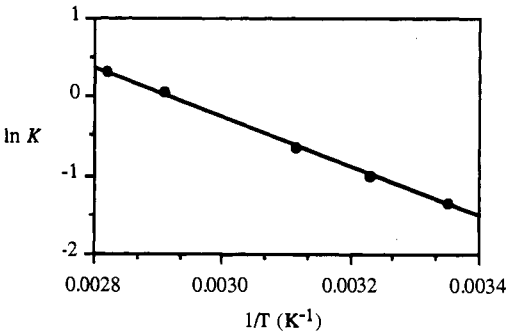
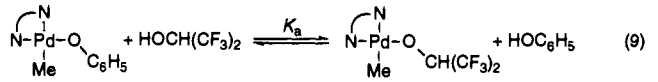


Figure 7. Van't Hoff plot for the equilibrium mixture of **1** and **3**.

We have further studied exchange reactions of HOCH(CF$_3$)$_2$ with the phenoxide ligand in [Pd(Me)(OC$_6$H$_5$)(tmeda)] (**3**). This phenoxide−alkoxide exchange leads to an equilibrium mixture of the methylpalladium complexes **1** and **3** (eq 9). The tem-



(9)

perature dependence of the equilibrium constants K_a for this reaction is shown in Figure 7, and the following thermodynamic parameters have been determined from this plot: $\Delta G° = 3.4 \pm 2.0$ kJ mol^{-1}, $\Delta H° = 26.5 \pm 1.5$ kJ mol^{-1}, and $\Delta S° = 77.4 \pm 4.2$ J K^{-1} mol^{-1}. Since the calculated equilibrium constant for this reaction ($-\log K_a = 0.7$), based on the acidity constants of phenol ($pK_a = 10.0$) and HOCH(CF$_3$)$_2$ ($pK_a = 9.3$), is similar to the measured $-\log K_a$ of 0.6, we conclude that this process is controlled by the acidity constants of the alcohols applied. For alkoxide−alcohol exchange two mechanisms are proposed in the literature: a dissociative pathway (A) and an associative pathway (B) (see Figure 8). The rate-limiting step in the dissociative pathway is the ionization of RO$^-$ from the palladium alkoxide complex if one assumes that recoordination of the alkoxide anion to the palladium center is fast.[21] Kinetic studies concerning platinum methoxide complexes have shown that

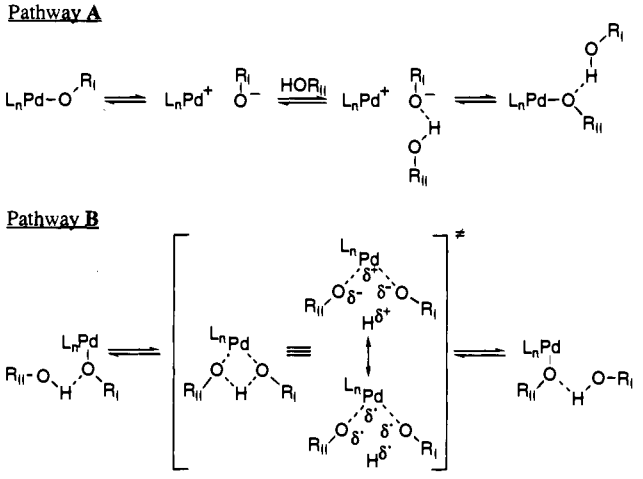


Figure 8. Mechanisms for the alkoxide—alcohol exchange process.

there is an upper limit for the rate of methoxide dissociation ($r = 10^{-7}$ s^{-1}; $\Delta G° > 110$ kJ mol^{-1}), and this means that the exchange process probably does not proceed by alkoxide dissociation for late transition metal alkoxides.[1c] Mechanistic studies concerning these thermoneutral exchange reactions have shown them to exhibit bimolecular kinetics over a wide range of conditions, and it has been concluded that exchange of alcohol and alkoxide is likely to involve an associative pathway for late transition metal alkoxides (pathway B; see Figure 8).[1c,21] Other evidence pointing to the involvement of an associative pathway is the fact that at low alcohol concentrations donor molecules can compete with the alcohol for the necessary open coordination site on the metal, thereby retarding the exchange process.[1c] An associative mechanism involves the formation of a five-coordinate transition state in the exchange process, and recently it has been suggested that this transition state (see Figure 8) has both hydrogen atom transfer and proton transfer character.[21] The ability of the methylpalladium alkoxide complexes **1**—**4** to form strong O—H···O hydrogen bonds to alcohols probably assists the formation of a five-coordinate species by holding the oxygen atom of the associated alcohol in the first coordination sphere of the metal center.

Concluding Remarks. The results presented in this paper serve to illustrate that chelating N-donor ligands are perfectly suitable for stabilizing organometallic palladium(II) species with alkoxide or aryloxide ligands. The ready accessibility and thermal stability of the complexes prepared emphasize a view that "unconventional" combinations of soft metal centers (*e.g.*, Pd(II) and hard ligands (*e.g.*, $^-$OR) are achievable with appropriate supporting ligand arrays. Although further studies are required to investigate the potential of these complexes in synthetic and catalytic processes, it is already clear that the tendency of such complexes to form adducts with alcohols is an important characteristic. Our thermodynamic data show O—H···O hydrogen bonds to be strong, and the linear relationship between $\Delta H°$ and $\Delta S°$ for adduct formation, which has parallels with organic systems, is a predictive tool that will be useful in understanding reactions of Pd—OR species with many organic compounds.

Experimental Section

General Considerations. Reactions were performed in an atmosphere of nitrogen using standard Schlenk techniques. 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 solvents acetone (pa), methanol (pa), and acetonitrile (pa) and the materials 1,1,1,3,3,3-hexafluoro-2-propanol, 2,2′-bipyridyl (bpy), phenol, *p*-nitrophenol, 2,4-dimethylphenol, catechol, and Celite (filter aid) were purchased from Janssen Chimica. The complexes [Pd(Me)$_2$(tmeda)],[17a,27] [Pd(Me)$_2$(bpy)],[17a,29] and [Pd(Me)(MeCN)(bpy)]BF$_4$[30] were prepared according to the literature. Sodium 1,1,1,3,3,3-hexafluoro-2-propoxide was prepared from 1,1,1,3,3,3-hexafluoro-2-propanol and NaH in THF. ^{1}H (300.13 MHz) and ^{13}C NMR (75.03 MHz) spectra were recorded on a Bruker AC 300 spectrometer at ambient temperature in deuterated solvents ($CDCl_3$, C_6D_6, and acetone-d_6) obtained from ISOTEC Inc. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

Synthesis of Methylpalladium(II) Alkoxides and Aryloxides and Their Adducts. Method A from Dimethylpalladium(II) Complexes. Preparation of [Pd(Me)(OCH(CF$_3$)$_2$)(tmeda)] (1). 1,1,1,3,3,3-Hexafluoro-2-propanol (0.56 mL, 5.3 mmol) was added dropwise to a solution of [Pd(Me)$_2$(tmeda)] (1.34 g, 5.3 mmol) in Et_2O (10 mL). The resulting yellow solution was stirred for 1 h, after which the solution was evaporated to dryness under reduced pressure. The yellow residue was washed twice with pentane (2 × 5 mL) and dried *in vacuo*. The residue was redissolved in Et_2O (10 mL) and filtered over Celite. The filtrate was evaporated to a small volume (ca. 3 mL), and the pure product **1** was obtained by slow diffusion of pentane into the Et_2O solution. The resulting yellow crystals were washed with pentane (2 × 5 mL) and dried *in vacuo*. Yield: 2.01 g (94%). Mp: 127 °C dec. ^{1}H NMR ($CDCl_3$): δ 4.00 (septet, 1H, $^3J_{H,F}$ = 7 Hz, OC*H*), 2.63—2.44 (m, 4H, C*H*$_2$C*H*$_2$), 2.55 (s, 6H, N(C*H*$_3$)$_2$), 2.47 (s, 6H, N(C*H*$_3$)$_2$), 0.21 (s, 3H, PdC*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 123.80 (q, $^1J_{C,F}$ = 290 Hz, *C*F$_3$), 75.08 (septet, $^2J_{C,F}$ = 30 Hz, O*C*H), 63.29 (N*C*H$_2$), 57.41 (N*C*H$_2$), 51.06 (N*C*H$_3$), 46.80 (N*C*H$_3$), −0.71 (Pd*C*H$_3$). Anal. Calcd for $C_{10}H_{20}F_6N_2OPd$: C, 29.68; H, 4.98; N, 6.92. Found: C, 29.86; H, 4.98; N, 6.87.

Preparation of [Pd(Me)(OCH(CF$_3$)$_2$)(bpy)] (2). To a suspension of [Pd(Me)$_2$(bpy)] (0.50 g, 1.7 mmol) in C_6H_6 (10 mL) was added 1,1,1,3,3,3-hexafluoro-2-propanol (0.18 mL, 1.7 mmol). The suspension turned gradually into a yellow solution which was filtered over Celite after 1 h. The solvent was evaporated from the filtrate, and the resulting yellow solid was washed with pentane (2 × 5 mL) and dried *in vacuo*. This afforded **2** as a pale yellow solid. Yield: 0.61 g (81%). Mp: 176 °C dec. ^{1}H NMR ($CDCl_3$): δ 8.94 (d, 1H, $^3J_{H,H}$ = 7 Hz, *H*$_6$), 8.65 (d, 1H, $^3J_{H,H}$ = 7 Hz, *H*′$_6$), 8.04—7.99 (m, 4H, *H*$_3$, *H*′$_3$, *H*$_4$, *H*′$_4$), 7.59 (td, 1H, $^3J_{H,H}$ = 7 Hz, $^4J_{H,H}$ = 1 Hz, *H*$_5$), 7.45 (td, 1H, $^3J_{H,H}$ = 7 Hz, $^4J_{H,H}$ = 1 Hz, *H*′$_5$), 4.34 (septet, 1H, $^3J_{H,F}$ = 7 Hz, OC*H*), 0.83 (s, 3H, PdC*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 157.19 (*C*$_2$), 152.29 (*C*′$_2$), 150.33 (*C*$_6$), 148.05 (*C*′$_6$), 138.45 (*C*$_5$), 137.96 (*C*′$_5$), 126.44 (*C*$_4$), 126.13 (*C*′$_4$), 122.25 (*C*$_3$), 120.73 (*C*′$_3$), 76.24 (septet, $^2J_{C,F}$ = 30 Hz, O*C*H), 3.69 (Pd*C*H$_3$). Anal. Calcd for $C_{17}H_{12}F_6N_2OPd$: C, 37.82; H, 2.72; N, 6.30. Found: C, 37.69; H, 2.67; N, 6.38.

Preparation of [Pd(Me)(OC$_6$H$_5$)(tmeda)] (3). Phenol (0.17 g, 1.8 mmol) was added to a solution of [Pd(Me)$_2$(tmeda)] (0.43 g, 1.7 mmol) in Et_2O (15 mL). After 1 h the product **3** which had precipitated was isolated by decantation, washed with pentane (2 × 5 mL), and dried *in vacuo*. Crystals suitable for a X-ray structure determination were obtained by slow diffusion of pentane into an Et_2O solution of **3**. The resulting pale yellow crystals were washed with pentane (2 × 5 mL) and dried *in vacuo*. Yield: 0.48 g (86%). Mp: 153 °C dec. ^{1}H NMR ($CDCl_3$): δ 7.03 (m, 4H, *o*,*m*-Ph), 6.40 (m, 1H, *p*-Ph), 2.65—2.41 (m, 4H, C*H*$_2$C*H*$_2$), 2.56 (s, 6H, N(C*H*$_3$)$_2$), 2.44 (s, 6H, N(C*H*$_3$)$_2$), 0.37 (s, 3H, PdC*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 168.80 (*ipso*-*C* Ph), 128.47 (*m*-*C* Ph), 120.33 (*o*-*C* Ph), 112.62 (*p*-*C* Ph), 63.29 (N*C*H$_2$), 57.20 (N*C*H$_2$), 50.91 (N*C*H$_3$), 47.62 (N*C*H$_3$), −3.47 (Pd*C*H$_3$). Anal. Calcd for $C_{13}H_{24}N_2OPd$: C, 47.21; H, 7.31; N, 8.47. Found: C, 47.28; H, 7.26; N, 8.41.

Preparation of [Pd(Me)(OC$_6$H$_4$-4-NO$_2$)(tmeda)] (4). The preparation of this complex was carried out using the procedure described above for **3**, employing *p*-nitrophenol as the reagent (2.10 mmol) and [Pd(Me)$_2$(tmeda)] (2.00 mmol). Crystals suitable for an X-ray structure determination were obtained by slow diffusion of pentane into an Et_2O solution of **4**. The resulting orange needles were washed with pentane (2 × 5 mL) and dried *in vacuo*. Yield: 0.61 g (82%). Mp: 172 °C dec. ^{1}H NMR (acetone-d_6): δ 7.98 (d, 2H, $^3J_{H,H}$ = 7 Hz, *m*-*H* Ar), 6.87 (d, $^3J_{H,H}$ = 7 Hz, *o*-*H* Ar), 2.75—2.55 (m, 4H, C*H*$_2$C*H*$_2$), 2.70 (s, 6H, N(C*H*$_3$)$_2$), 2.49 (s, 6H, N(C*H*$_3$)$_2$), 0.43 (s, 3H, PdC*H*$_3$). ^{13}C NMR (acetone-d_6): δ 176.42 (*ipso*-*C* Ar), 126.41 (*m*-*C* Ar), 126.17 (*o*-*C* Ar),

(29) Byers, P. K.; Canty, A. J. *Organometallics* **1990**, *9*, 210.
(30) Byers, P. K.; Skelton, B. W.; White, A. H.; Canty, A. J. *J. Organomet. Chem.* **1990**, *393*, 299.

116.07 (*p-C* Ar), 63.59 (NCH_2), 57.19 (NCH_2), 51.23 (NCH_3), 47.65 (NCH_3), −2.54 ($PdCH_3$). Anal. Calcd for $C_{13}H_{23}N_3O_3Pd$: C, 41.55; H, 6.17; N, 11.18. Found: C, 41.95; H, 6.00; N, 10.89.

Preparation of [Pd(Me)(OCH(CF$_3$)$_2$)(tmeda)]·HOCH(CF$_3$)$_2$ (5). Complex **5** was obtained as a pale yellow solid using the procedure described for **1**, employing 2 equiv of 1,1,1,3,3,3-hexafluoro-2-propanol as the reagent. Yield: 88% (1.8 mmol scale). Mp: 129 °C dec. ^{1}H NMR ($CDCl_3$): δ 4.57 (septet, 1H, $^3J_{H,F}$ = 7 Hz, HOC*H*), 4.05 (septet, 1H, $^3J_{H,F}$ = 7 Hz, PdOC*H*), 2.65−2.42 (m, 4H, CH_2CH_2), 2.58 (s, 6H, $N(CH_3)_2$), 2.47 (s, 6H, $N(CH_3)_2$), 0.28 (s, 3H, $PdCH_3$). ^{13}C NMR (C_6D_6): δ 124.10 (q, $^1J_{C,F}$ = 290 Hz, *C*F$_3$), 122.90 (q, $^1J_{C,F}$ = 290 Hz, *C*F$_3$), 75.36 (septet, $^2J_{C,F}$ = 30 Hz, PdO*C*H), 69.28 (septet, $^2J_{C,F}$ = 30 Hz, HO*C*H), 62.30 (NCH_2), 56.71 (NCH_2), 50.08 (NCH_3), 46.50 (NCH_3), −0.72 ($PdCH_3$). Anal. Calcd for $C_{13}H_{22}F_{12}N_2O_2Pd$: C, 27.26; H, 3.87; N, 4.89. Found: C, 27.33; H, 3.95; N, 4.97.

Preparation of [Pd(Me)(OCH(CF$_3$)$_2$)(bpy)]·HOCH(CF$_3$)$_2$ (6). Complex **6** was obtained as a yellow solid using the procedure described for **2**, employing 2 equiv of 1,1,1,3,3,3-hexafluoro-2-propanol as the reagent. Yield: 79% (1.5 mmol scale). Mp: 175 °C dec. ^{1}H NMR ($CDCl_3$): δ 8.84 (d, 1H, $^3J_{H,H}$ = 7 Hz, *H*$_6$), 8.61 (d, 1H, $^3J_{H,H}$ = 7 Hz, *H*′$_6$), 8.06−7.98 (m, 4H, *H*$_3$, *H*′$_3$, *H*$_4$, *H*′$_4$), 7.58 (td, 1H, $^3J_{H,H}$ = 7 Hz, $^4J_{H,H}$ = 1 Hz, *H*$_5$), 7.47 (td, 1H, $^3J_{H,H}$ = 7 Hz, $^4J_{H,H}$ = 1 Hz, *H*″$_5$), 4.66 (septet, 1H, $^3J_{H,F}$ = 7 Hz, HO*C*H), 4.34 (septet, 1H, $^3J_{H,F}$ = 7 Hz, PdO*C*H), 0.84 (s, 3H, $PdCH_3$). ^{13}C NMR (acetone-*d*$_6$): δ 157.92 (*C*$_2$), 153.73 (*C*′$_2$), 151.08 (*C*$_6$), 147.74 (*C*′$_6$), 140.22 (*C*$_5$), 139.74 (*C*′$_5$), 127.68 (*C*$_4$), 127.25 (*C*′$_4$), 124.27 (*C*$_3$), 122.83 (*C*′$_3$), 76.90 (septet, $^2J_{C,F}$ = 30 Hz, PdO*C*H), 69.34 (septet, $^2J_{C,F}$ = 30 Hz, HO*C*H), 3.55 ($PdCH_3$). Anal. Calcd for $C_{17}H_{14}F_{12}N_2O_2Pd$: C, 33.33; H, 2.30; N, 4.57. Found: C, 33.30; H, 2.39; N, 4.61.

Preparation of [Pd(Me)(OC$_6$H$_5$)(tmeda)]·HOC$_6$H$_5$ (7). Complex **7** was obtained as a yellow solid using the procedure described for **3**, employing 2 equiv of phenol as the reagent. Crystals of **7** (suitable for an X-ray structure determination) were obtained by slow diffusion of pentane into an Et_2O solution. The resulting yellow needles were washed with pentane (2 × 5 mL) and dried *in vacuo*. Yield: 92% (1.8 mmol scale). Mp: 154 °C dec. ^{1}H NMR ($CDCl_3$): δ 9.1 (br s, 1H, O*H*), 7.23−7.03 (m, 8H, *o,m-H* of PdOPh and HOPh), 6.84 (t, 1H, $^3J_{H,H}$ = 7 Hz, *p-H* HOPh), 6.49 (t, 1H, $^3J_{H,H}$ = 7 Hz, *p-H* PdOPh), 2.72−2.46 (m, 4H, CH_2CH_2), 2.66 (s, 6H, $N(CH_3)_2$), 2.50 (s, 6H, $N(CH_3)_2$), 0.45 (s, 3H, $PdCH_3$). ^{13}C NMR ($CDCl_3$): δ 167.38 (*ipso-C* PdOPh), 158.18 (*ipso-C* HOPh), 129.22 (*m-C* PdOPh), 128.58 (*m-C* HOPh), 120.21 (*o-C* PdOPh), 118.56 (*p-C* HOPh), 116.24 (*o-C* HOPh), 113.70 (*p-C* PdOPh), 63.36 (NCH_2), 57.26 (NCH_2), 51.02 (NCH_3), 47.65 (NCH_3), −2.76 ($PdCH_3$). Anal. Calcd for $C_{19}H_{30}N_2O_2Pd$: C, 53.71; H, 7.12; N, 6.59. Found: C, 53.77; H, 7.19; N, 6.65.

Preparation of [Pd(Me)(OC$_6$H$_4$-4-NO$_2$)(tmeda)]·HOC$_6$H$_4$-4-NO$_2$ (8). Complex **8** was obtained as a yellow solid using the procedure described for **2**, employing 2 equiv of *p*-nitrophenol as the reagent. Crystals of **8** (suitable for an X-ray structure determination) were obtained by slow diffusion of pentane into an Et_2O solution. The resulting orange crystals were washed with pentane (2 × 5 mL) and dried *in vacuo*. Yield: 79% (1.7 mmol scale). Mp: 170 °C. ^{1}H NMR (acetone-*d*$_6$): δ 8.17 (d, 2H, $^3J_{H,H}$ = 7 Hz, *m-H* HOAr), 7.93 (d, 2H, $^3J_{H,H}$ = 7 Hz, *m-H* PdOAr), 7.05 (d, 2H, $^3J_{H,H}$ = 7 Hz, *o-H* HOAr), 6.89 (d, 2H, $^3J_{H,H}$ = 7 Hz, *o-H* PdOAr), 2.84−2.87 (m, 2H, CH_2), 2.67−2.64 (m, 2H, CH_2), 2.70 (s, 6H, $N(CH_3)_2$), 2.46 (s, 6H, $N(CH_3)_2$), 0.29 (s, 3H, $PdCH_3$). Anal. Calcd for $C_{19}H_{28}N_4O_6Pd$: C, 44.32; H, 5.48; N, 10.88. Found: C, 44.40; H, 5.44; N, 10.79.

The non-alcohol-associated complexes **1**−**4** cannot be regenerated from the adducts **5**−**8** by washing the latter complexes with Et_2O or pentane. Heating the complexes **5**−**8** to 40 °C *in vacuo* for 24 h also did not lead to loss of the hydrogen-bonded alcohol molecule to produce the complexes **1**−**4**.

Preparation of [Pd(Me)(OC$_6$H$_5$)(bpy)]·HOC$_6$H$_5$ (9). Phenol (0.42 g, 4.5 mmol) was added to a solution of [Pd(Me)$_2$(bpy)] (0.65 g, 2.6 mmol) in CH_2Cl_2 at 0 °C. The solution turned gradually yellow, and after 1 h the solvent was evaporated. The resulting yellow solid was washed twice with pentane (2 × 5 mL) and dried *in vacuo*. Yield: 0.91 g (75%). Mp: >200 °C. ^{1}H NMR ($CDCl_3$): δ 8.20−7.00 (m, 8H, bpy), 7.30−7.02 (m, 8H, *o,m-H* of PdOPh and HOPh), 7.1 (br s, 1H, O*H*), 6.83 (t, 1H, $^3J_{H,H}$ = 7 Hz, *p-H* HOPh), 6.58 (t, 1H, $^3J_{H,H}$ = 7 Hz, *p-H* PdOPh), 0.93 (s, 3H, $PdCH_3$). ^{13}C NMR (acetone-*d*$_6$): δ 167.50 (*ipso-C* PdOPh), 158.44 (*ipso-C* HOPh), 157.97 (*C*$_2$), 153.81 (*C*′$_2$), 151.02 (*C*$_6$), 148.78 (*C*′$_6$), 140.26 (*C*$_5$), 140.03 (*C*′$_5$), 130.19 (*m-C* PdOPh), 129.17 (*m-C* HOPh), 127.81 (*C*$_4$), 127.60 (*C*′$_4$), 124.28 (*C*$_3$), 122.03 (*C*′$_3$), 121.11 (*o-C* PdOPh), 120.01 (*o-C* HOPh), 116.13 (*o-C* of HOPh and PdOPh), 0.34 ($PdCH_3$). Anal. Calcd for $C_{23}H_{22}N_2O_2Pd$: C, 59.43; H, 4.77; N, 6.03. Found: C, 59.31; H, 4.85; N, 6.09.

Preparation of [Pd(Me)(OC$_6$H$_3$-2,4-Me$_2$)(tmeda)]·HOC$_6$H$_3$-2,4-Me$_2$ (10). Complex **10** was obtained as a yellow solid using the procedure described for **3**, employing 2 equiv of 2,4-dimethylphenol as the reagent. Yield: 83% (1.0 mmol scale). Mp: 156 °C dec. ^{1}H NMR (C_6D_6): δ 7.65 (d, 1H, $^3J_{H,H}$ = 7 Hz), 7.11 (s, 1H), 6.98 (d, 1H, $^3J_{H,H}$ = 7 Hz), 6.86 (d, 1H, $^3J_{H,H}$ = 7 Hz), 6.84 (d, 1H, $^3J_{H,H}$ = 7 Hz), 2.70 (s, 6H, $N(CH_3)_2$), 2.68 (s, 3H, ArCH_3), 2.49 (s, 3H, ArCH_3), 2.46 (s, 6H, $N(CH_3)_2$), 2.30 (s, 3H, ArCH_3), 2.18 (s, 3H, ArCH_3), 1.41−1.30 (m, 4H, CH_2), 0.71 (s, 3H, $PdCH_3$). Anal. Calcd for $C_{23}H_{38}N_2O_2Pd$: C, 57.43; H, 7.96; N, 5.82. Found: C, 57.49; H, 7.88; N, 5.80.

Preparation of [Pd(Me)(OC$_6$H$_4$-2-OH)(tmeda)] (11). Catechol (0.33 g, 3.0 mmol) was added to a solution of [Pd(Me)$_2$(tmeda)] (0.70 g, 2.8 mmol) in Et_2O (15 mL). After 1 h the product, which had precipitated as a white solid, was isolated by decantation, washed twice with pentane (2 × 5 mL), and dried *in vacuo*. Yield: 0.87 g (90%). Mp: >200 °C. ^{1}H NMR ($CDCl_3$): δ 7.16 (d, 1H, $^3J_{H,H}$ = 7 Hz, Ar*H*), 6.71 (d, 1H, $^3J_{H,H}$ = 7 Hz, Ar*H*), 6.70 (br s, 1H, O*H*), 6.63 (t, 1H, $^3J_{H,H}$ = 7 Hz, Ar*H*), 6.38 (t, 1H, $^3J_{H,H}$ = 7 Hz, Ar*H*), 2.70−2.40 (m, 4H, CH_2CH_2), 2.65 (s, 6H, $N(CH_3)_2$), 2.47 (s, 6H, $N(CH_3)_2$), 0.41 (s, 3H, $PdCH_3$). ^{13}C NMR ($CDCl_3$): δ 155.23 (*ipso-C* Ar), 148.66, 119.40, 118.39, 113.62, 111.07, 63.41 (NCH_2), 57.21 (NCH_2), 51.08 (NCH_3), 47.54 (NCH_3), −2.95 ($PdCH_3$). Anal. Calcd for $C_{13}H_{24}N_2O_2Pd$: C, 45.03; H, 6.98; N, 8.08. Found: C, 45.08; H, 6.88; N, 7.95.

Method B from Cationic Alkylpalladium(II) Complexes. Preparation of [Pd(Me)(OCH(CF$_3$)$_2$)(bpy)] (2). To a solution of [Pd(Me)(MeCN)(bpy)]BF_4 (0.24 g, 0.59 mmol) in acetone (10 mL) was added a solution of sodium 1,1,1,3,3,3-hexafluoro-2-propoxide (0.11 g, 0.58 mmol) in acetone (2 mL). The clear solution turned immediately yellow. After 5 min, the solution was evaporated to dryness, the yellow residue extracted with CH_2Cl_2, and the extract filtered over Celite. The yellow filtrate was evaporated to dryness, and the resulting yellow solid was washed with pentane (2 × 5 mL) and dried *in vacuo*. This afforded the product **2** in a yield of 0.22 g (85%).

Method C. Ligand Exchange Starting from [Pd(Me)(OCH(CF$_3$)$_2$)(tmeda)] (1). Preparation of [Pd(Me)(OCH(CF$_3$)$_2$)(bpy)] (2). To a stirred solution of [Pd(Me)(OCH(CF$_3$)$_2$)(tmeda)] (**1**) (0.48 g, 1.2 mmol) dissolved in a minimum of acetone (5 mL) was added 4 equiv of bpy (0.75 g, 4.8 mmol). After 1 h, Et_2O was added, and the precipitated solid was isolated by decantation. This residue was washed with Et_2O and crystallized from acetone/pentane at −20 °C, affording yellow needles of pure **2**. Yield: 0.31 g (58%).

Preparation of [Pd(Me)(OCH(CF$_3$)$_2$)(Ph$_2$PCH$_2$CH$_2$NMe$_2$)] (12). This complex was prepared using the procedure described for **2** (method C) employing $Ph_2PCH_2CH_2NMe_2$ (0.33 g, 1.3 mmol) and [Pd(Me)(OCH(CF$_3$)$_2$)(tmeda)] (**1**) (0.48 g, 1.2 mmol). Yield: 0.59 g (91%). ^{1}H NMR (acetone-*d*$_6$): δ 7.79−7.63 (m, 4H, Ar), 7.60−7.48 (m, 6H, Ar), 4.48 (septet, 1H, $^3J_{HF}$ = 6.5 Hz, OC*H*), 2.75−2.50 (m, 4H, CH_2CH_2), 2.60 (s, 6H, NCH_3), 0.15 (d, 3H, $^3J_{HP}$ = 1.2 Hz, $PdCH_3$). ^{13}C NMR (acetone-*d*$_6$): δ 134.09 (d, $^2J_{CP}$ = 12 Hz, *m-C* Ar), 132.02 (*p-C* Ar), 131.42 (d, $^1J_{CP}$ = 50 Hz, *ipso-C* Ar), 129.80 (d, $^3J_{CP}$ = 11 Hz, *o-C* Ar), 125.62 (q, $^1J_{CF}$ = 286 Hz, *C*F$_3$), 74.98 (septet, $^2J_{CF}$ = 29 Hz, O*C*H), 59.34 (d, $^2J_{CP}$ = 5 Hz, NCH_2), 47.48 (NCH_3), 31.35 (d, $^1J_{CP}$ = 12 Hz, PCH_2), −3.24 (d, $^2J_{CP}$ = 7.5 Hz). Anal. Calcd for $C_{20}H_{24}F_6ONPPd$: C, 44.01; H, 4.43; N, 2.57. Found: C, 44.16; H, 4.42; N, 2.67.

Preparation of [Pd(Me)(OCH(CF$_3$)$_2$)(dppe)] (13). This complex was prepared using the procedure described for **2** (method C) employing dppe (0.13 g, 0.32 mmol) and [Pd(Me)(OCH(CF$_3$)$_2$)(tmeda)] (**1**) (0.11 g, 0.29 mmol). Yield: 0.16 g (85%). NMR data: similar to those reported.[10a]

Preparation of *trans*-[Pd(Me)(OCH(CF$_3$)$_2$(PMe$_3$)$_2$] (14). A solution of PMe_3 in toluene (0.78 mmol) was added to a solution of [Pd(Me)(OCH(CF$_3$)$_2$)(tmeda)] (**1**) (0.14 g, 0.37 mmol) in toluene. After 1 h, the solution was evaporated to dryness, and the residue was washed with pentane (2 × 5 mL) and dried *in vacuo*. Yield: 0.13 g (78%). NMR data: similar to those reported.[10a]

Association of Alcohol and Phenol with Alkoxide and Aryloxide Complexes. Synthesis of Methylpalladium(II) Alkoxides and Aryl-

Table 4. Crystallographic Data for **1**, **3**, **4**, **7**, and **8**

complex	**1**	**3**	**4**	**7**	**8**
			Crystal Data		
formula	$C_{10}H_{20}F_6N_2OPd$	$C_{13}H_{24}N_2OPd$	$C_{13}H_{23}N_3O_3Pd$	$C_{13}H_{24}N_2OPd{\cdot}C_6H_6O$	$C_{13}H_{23}N_3O_3Pd{\cdot}C_6H_5NO_3$
molecular weight	404.69	330.77	375.76	424.88	514.87
crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$ (no. 14)	*Pbca* (no. 61)	*Pbca* (no. 61)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a (Å)	8.2054(5)	10.572(2)	11.918(5)	15.5556(13)	8.7029(5)
b (Å)	17.2310(9)	16.446(2)	12.089(3)	11.0416(10)	15.6384(11)
c (Å)	11.1191(12)	17.029(3)	22.684(7)	12.0211(11)	16.5188(9)
β (deg)	105.701(7)			91.343(8)	90.096(5)
V (Å^3)	1513.4(2)	2960.8(8)	3268(2)	2064.2(3)	2248.2(2)
D_{calc} (g cm^{-3})	1.776	1.484	1.527	1.367	1.521
Z	4	8	8	4	4
F(000)	808	1360	1536	880	1056
μ (cm^{-1})	12.7	12.3	94.8	75.1	8.5
crystal size (mm)	0.08 × 0.15 × 0.80	0.1 × 0.3 × 0.3	0.3 × 0.3 × 0.1	0.04 × 0.65 × 1.23	0.3 × 0.3 × 0.5
			Data Collection		
T(K)	150	298	298	298	298
θ_{min}, θ_{max} (deg)	1.2, 27.5	1.2, 27.5	2.0, 75.0	2.9, 75.0	1.2, 27.5
SET4 θ_{min}, θ_{max} (deg)	10.6, 14.0	11.4, 13.9	16.7, 23.6	17.8, 24.2	9.0, 15.7
wavelength (Å)	0.710 73 (Mo Kα) (graphite monochromator)	0.710 73 (Mo Kα) (graphite monochromator)	1.541 84 (Cu Kα) (Ni filter)	1.541 84 (Cu Kα) (Ni filter)	0.710 73 (Mo Kα) (Zr filter)
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
$\Delta\omega$ (deg)	1.04 + 0.35 tan θ	0.56 + 0.35 tan θ	1.35 + 0.14 tan θ	0.62 + 0.14 tan θ	0.51 + 0.35 tan θ
horiz, vert apertures, (mm)	4.06, 4.00	3.00, 4.00	5.31, 6.00	3.00, 6.00	3.00, 5.00
X-ray exposure time (h)	20	28	70	131	139
linear decay (%)	1	0	4	45	1
reference reflections	$\bar{2}\bar{2}3$, $4\bar{2}\bar{2}$, $3\bar{3}\bar{2}$	$\bar{4}02$, $\bar{3}21$, $\bar{2}2\bar{5}$	$\bar{2}3\bar{3}$, 027, $\bar{5}0\bar{2}$	$22\bar{4}$, $23\bar{2}$, $2\bar{3}\bar{2}$	$\bar{2}2\bar{3}$, $2\bar{2}\bar{5}$, $\bar{1}\bar{5}\bar{2}$
data set	−10:10, −22:0, −14:11	−13:13, 0:21, −22:22	−14:0, 0:15, −28:28	−19:19, −13:13, −15:15	−11:11, −20:0, −21:21
total no. of data	5797	14 751	7277	16 415	10 748
total unique data	3469	3385	3293	4250	5146
absorption corr range	0.87, 1.06 (DIFABS)	0.86, 1.27 (DIFABS)	0.78, 1.47 (DIFABS)	1.37, 15.5 (ABSORB)	0.75, 1.20 (DIFABS)
			Refinement		
no. of refined params	189	159	186	223	279
final $R1$[a]	0.023 [2935$F_o > 4\sigma(F_o)$]	0.0450 [2297$F_o > 4\sigma(F_o)$]	0.0441 [2307$F_o > 4\sigma(F_o)$]	0.0281 [3933$F_o > 4\sigma(F_o)$]	0.0361 [3209$F_o > 4\sigma(F_o)$]
final $wR2$[b]	0.057	0.102	0.099	0.064	0.088
goodness of fit	1.03	1.03	1.04	1.11	0.94
w^{-1} [c]	$\sigma^2(F^2) + (0.0295P)^2 + 0.57P$	$\sigma^2(F^2) + (0.0488P)^2$	$\sigma^2(F^2) + (0.0408P)^2$	$\sigma^2(F^2) + (0.0149P)^2 + 0.51P$	$\sigma^2(F^2) + (0.0410P)^2$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.000, 0.002	0.000, 0.003	0.001, 0.010	0.000, 0.002	0.001, 0.012
min and max residual density, e Å^{-3}	−0.47, 0.60	−0.70, 0.48	−0.50, 0.45	−0.60, 0.41	−0.44, 0.57

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

oxides. Method D. Preparation of [Pd(Me)($OCH(CF_3)_2$)(tmeda)]·$HOCH(CF_3)_2$ (5). To a solution of **1** (0.25 g, 0.62 mmol) in Et_2O (5 mL) was added less than 1 equiv of 1,1,1,3,3,3-hexafluoro-2-propanol (0.09 g, 0.54 mmol). The solution was saturated with pentane and stored at −20 °C for 24 h to provide crystals of **5**. The crystals were collected by decantation, washed with pentane (2 × 5 mL), and dried *in vacuo*. Yield: 0.31 g (88%).

Preparation of [Pd(Me)($OCH(CF_3)_2$)(bpy)]·$HOCH(CF_3)_2$ (6). This complex was prepared using the procedure described for **5** (method D) employing complex **2** (0.58 g, 1.3 mmol) and 1,1,1,3,3,3-hexafluoro-2-propanol (0.13 mL, 1.2 mmol). Yield: 0.65 g (82%).

Preparation of [Pd(Me)(OC_6H_5)(tmeda)]·HOC_6H_5 (7). This complex was prepared using the procedure described for **5** (method D) employing complex **1** (0.20 g, 0.50 mmol) and phenol (0.04 g, 0.45 mmol). Yield: 0.18 g (85%).

Physical Measurements. Intramolecular Alkoxide−Alcohol Exchange. Rates, $1/\tau$, for the two-site alkoxide (H_a)−alcohol (H_b) exchange process in the O−H···O hydrogen-bonded complex [Pd(Me)($OCH(CF_3)_2$)(tmeda)]·$HOCH(CF_3)_2$ (**5**) in $CDCl_3$ have been measured by ^1H NMR spin saturation transfer (200 MHz; presaturation time, 25 s; relaxation delay, 25 s; 90° pulse, 8 μs) using the Forsén−Hoffman method.[28] Spectra were measured at four different temperatures (calibrated externally against CH_3OH). Rates were determined with use of the expression $1/\tau = (1/T_{1b})[(M_0/M_\infty) - 1]$ where T_{1b} is the spin−lattice relaxation time of the proton of the coordinated $OCH(CF_3)_2$ unit, M_0 is the normal equilibrium magnetization, and M_∞ is the equilibrium magnetization of proton B after saturating the CH proton resonance of site A. T_{1a} and T_{1b} values have been measured by the inversion−recovery Fourier transform (IRFT) method (10 data sets, 90° (180°) pulse width of 8 (16) μs, relaxation delay of 25 s, 8 scans per data set) with the well-known sequence $[180°-\tau-90°-(\text{acquisition})-T]_n$.

Determination of Association Constants. Four NMR samples containing 1,1,1,3,3,3-hexafluoro-2-propanol or phenol at a fixed concentration (0.012 or 0.010 M, respectively) in $CDCl_3$ (dried on anhydrous $CaCl_2$) with accurately weighed amounts of palladium alkoxide complex **1** or aryloxide complex **3** were prepared so as to give concentrations in the range 0.094−0.335 M. The chemical shift of the OH proton was measured at four different temperatures for each sample. The OH chemical shift of 1,1,1,3,3,3-hexafluoro-2-propanol or phenol in $CDCl_3$ without added palladium alkoxide or aryloxide was also determined at each temperature. The microscopic association constant k_{ass} is calculated at each temperature using the Scatchard equation[22] (eq 10), where $\delta(OH)_{obs}$ is the observed chemical shift of

$$\frac{\delta(OH)_{obs} - \delta(OH)_{alc}}{c_{Pd-OR}} = -k_{ass}\{\delta(OH)_{obs} - \delta(OH)_{alc}\} + Z \qquad (10)$$

the OH signal, $\delta(OH)_{alc}$ is the chemical shift of free, uncomplexed alcohol, c_{Pd-OR} is the concentration of **1** or **3** based on the weighed amount of palladium alkoxide or aryloxide complex, and Z is a constant. These measurements have been done in duplicate and were found to be highly reproducible.

Structure Determination and Refinement of 1, 3, 4, 7, and 8. Crystals of **1**, **3**, **4**, **7**, and **8**, suitable for X-ray diffraction, were glued onto the tip of a glass fiber and transferred to an Enraf-Nonius CAD4-T diffractometer on a rotating anode (**1** and **3**) or to an Enraf-Nonius CAD4-F diffractometer with a sealed tube (**4**, **7**, and **8**). Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of the setting angles of 25 well-centered reflections (SET4). Reduced-cell calculations did not indicate higher lattice symmetry.[31] Crystal data and details on data collection and refinement are collected in Table 4. Data were corrected for L*p* effects and for the observed linear decay of the reference reflections. An analytical absorption correction, based on Gaussian integration techniques (ABSORB)[32] was applied for compound **7**; empirical absorption correction was applied for compounds **1**, **3**, **4**, and **8** (DIFABS).[33] F_c values of **1** were corrected for secondary extinction by refinement of an empirical isotropic parameter: $F'_c = F_c[1 + xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$, with $x = 2.8(3) \times 10^{-6}$. The structures were solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIR-92[34] for **1**, **3**, and **8** and SHELXS86[35] for **4** and **7**). All structures were refined on F^2 using full-matrix least-squares techniques (SHELXL-93);[36] no observance criterion was applied during refinement. Hydrogen atoms were included in the refinement on calculated positions, riding on their carrier atoms, except for the hydroxyl hydrogen of **8**, which was located on a difference Fourier map and subsequently included in the refinement. The hydroxyl hydrogen of **7** was located on a circular Fourier map around O(2) and refined as a rigid group allowing for rotation around the C−O bond. All methyl hydrogen atoms were refined in a rigid group, allowing for rotation around the N−C or Pd−C bonds. The non-hydrogen atoms of all structures were refined with anisotropic thermal parameters. The hydrogen atoms of **1** were refined with two overall isotropic thermal parameters with values of 0.042(2) Å^2 for the hydrogen atoms of the methyl groups and 0.039(3) Å^2 for the other hydrogen atoms. The hydrogen atoms of the other complexes 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 of 1.5 for the methyl and hydroxyl 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*.[37] Geometrical calculations and illustrations were performed with PLATON;[38] all calculations were performed on a DECstation 5000 cluster.

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Supporting Information Available: Tables giving further details of the structure determinations, including atomic coordinates, bond lengths and angles, and thermal parameters **1**, **3**, **4**, **7**, and **8** and ORTEP (30% probability level) drawings of the molecular structures of complexes **3** and **7** (29 pages); listings of observed and calculated structure factor amplitudes for **1**, **3**, **4**, **7**, and **8** (44 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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