Arylpalladium Compounds Containing an Alcohol Functionality: Hindered Rotation around the Pd–C Bond and Reactivity toward Styrene and Carbon Monoxide. Comments on C–O Bond Shortening in Late-Transition-Metal Alkoxides

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Received September 30, 1992

The arylpalladium bromide complex PdBr{$C_6H_4(CH_2CH_2OH)$-2}(tmeda) (1) was prepared from 2-(2-bromophenyl)ethanol and $Pd(dba)_2$ in the presence of tmeda. The crystal structure of 1 shows a square plane surrounding palladium with the aryl ring positioned nearly perpendicular to the square-planar coordination plane and the alcoholic hydroxyl group intramolecularly hydrogen bonded to the bromide ligand. Crystals of 1 are monoclinic, space group *Cc*, with a = 12.412(1) Å, b = 10.391(1) Å, c = 13.441(1) Å, β = 106.43(1)°, Z = 4, and R = 0.024 for 1872 reflections with $I > 2.5\sigma(I)$ and 188 parameters. The ^1H and ^{13}C NMR spectra of 1 in $CDCl_3$ show that the lack of symmetry found in the crystal structure is retained (on the NMR time scale) up to 60 °C. In methanol, however, the ^1H NMR spectra of 1 show fluxional behavior, and at 60 °C the data are consistent with the presence of an (apparent) plane of symmetry coinciding with the square coordination plane around palladium. Evidence is given that this results from rapid rotation of the aryl ring around the Pd–C(ipso) bond. The rotation is induced by an intramolecular substitution of the hydroxyl group for the bromide anion (i.e. ionization). Halide abstraction from 1 with $AgNO_3$ gives the ionic complex [Pd{$C_6H_4(CH_2CH_2OH)$-2}(tmeda)]-NO_3 (3), whose structure has been confirmed by a single-crystal X-ray study. Crystals of 3 are orthorhombic, space group $P2_1ab$, with a = 9.679(1) Å, b = 11.903(2) Å, c = 14.501(2) Å, Z = 4, and R = 0.0245 for 1635 reflections with $I > 2.5\sigma(I)$ and 215 parameters. In the cation, the hydroxyl group is O-bonded to palladium to form a six-membered chelate ring. The NMR spectra of 3 indicate that this structure is retained in solution both in dichloromethane and methanol or water. Aqueous solutions of 3 are weakly acidic, and the alkoxide Pd{$C_6H_4(CH_2CH_2O)$-2}(tmeda) (4) is formed upon deprotonation of 3 with potassium methoxide. The intramolecular bonding of the alcoholic group in 3 is readily disrupted by pyridine, and the lability of the Pd–O bond also accounts for the high reactivity of 3 toward styrene and carbon monoxide. The effect of molecular structure on the C–O bond length in late-transition-metal alkoxides is discussed. It is concluded that the C–O bond and O–C–C tilt angle in these alkoxides respond qualitatively in the same way to variation in the M–O–C–C torsion angle as is theoretically predicted for the corresponding alcohol. The short C–O bond generally observed in these compounds is more likely an intrinsic property of alkoxide anions rather than a reflection of any tendency to decompose via β-elimination.

Introduction

Whereas the organometallic chemistry of the platinum metals has been extensively investigated during the last few decades, interest in the chemistry of late-transition-metal alkoxides and amides is of a much more recent date.[1] This intuitively reversed order of research activity reflects the relative instability of late-transition-metal alkoxides (and amides) compared to the corresponding alkyl derivatives. For example, whereas the platinum dimethoxide complex [$Pt(OMe)_2$(dppe)] (dppe = 1,2-bis(diphenylphosphino)ethane) decomposes rapidly already at room temperature, the analogous dialkyl compound [$PtEt_2$(dppe)] requires temperatures in excess of 150 °C for slow decomposition.[2] The instability of late-transition-metal alkoxides has been explained in terms of a mismatch between the "hard" oxygen donor and the "soft" metal acceptor.[3] At a somewhat higher level, it has been suggested that the instability arises from antibonding π-interactions between the lone pairs on the oxygen atom and the filled metal d orbitals.[4] Both explanations suggest an intrinsically lower thermodynamic stability of the M–O over the M–C bond for these metals. However, both experimental comparison of Pt–Nu (Nu = CR_3, NR_2, OR)

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(3) For a review on complexes of the platinum metals containing weak donor ligands, see: Davies, J. A.; Hartley, F. R. *Chem. Rev.* 1981, *81*, 79.

(4) (a) Mayer, J. M. *Comments Inorg. Chem.* 1988, *8*, 125. (b) Very recently, evidence for alkoxide π-donation to iridium(III) has been obtained: Lunder, D. M.; Lobkovsky, E. B.; Streib, W. E.; Caulton, K. G. *J. Am. Chem. Soc.* 1991, *113*, 1837.

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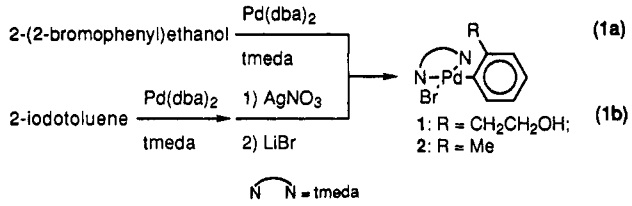
bond strengths[5] and theoretical calculations of bond strengths in $PdNu_2$ (Nu = H, CH_3, OH, OMe, F) systems[6] show that the metal–oxygen bond is actually comparable in strength to or stronger than the metal–carbon bond. Therefore, the observed instability of late-transition-metal alkoxides is of kinetic rather than thermodynamic origin.

In fact, by using appropriate ligands and suitably substituted alkoxide groups, several stable alkoxides of Pt, Ir, Rh, and Pd have recently been prepared by a number of groups. The rich chemistry exhibited by these species, such as insertion reactions into the metal–oxygen bond,[7,11] deprotonation of active methyl compounds,[8] β-hydride elimination,[2,9] C–O bond formation,[10] and C–H activation,[11] not only merits study in its own right but is also relevant for the elucidation of the mechanism of several catalytic reactions in which alkoxides have been postulated as intermediates.[12]

In the course of our studies on C–O coupling reactions of alcohols to organopalladium compounds we became interested in organopalladium compounds which contain an alcoholic group close to the metal center.[13] In this paper we describe the synthesis of the arylpalladium bromide 1, which contains an alcoholic side chain attached to the aryl ring in the ortho position. The fluxional behavior of 1 in alcoholic solvents is discussed. The neutral palladium bromide 1 can be converted by halide abstraction with $AgNO_3$ into the ionic complex 3, which is one of the very rare isolated examples of a palladium compound with a coordinated alcohol functionality.[3,14] Reactions of this remarkably stable species with Lewis bases, styrene, and carbon monoxide are described. The compound can be deprotonated to the corresponding alkoxide 4, which is a palladium compound with a chelate-bonded C,O dianionic ligand. Finally, the crystal structures of compounds 1 and 3 are discussed and reference is made to some other structures of late-transition-metal alkoxides. It is pointed out that late-transition-metal alkoxides obey theoretical ideas on structural features of (isolated) alkoxide anions, due to their monomeric nature and high polarity of the metal–oxygen bond.

Results and Discussion

Preparation and Fluxional Behavior of 1. Oxidative addition of 2-(2-bromophenyl)ethanol to $Pd(dba)_2$ (dba = dibenzylideneacetone) in the presence of tmeda (tmeda = *N,N,N′,N′*-tetramethylethane-1,2-diamine) (eq 1a) affords the arylpalladium bromide 1 in 58% yield as a yellow-orange powder, which is very soluble in chlorinated solvents (CH_2Cl_2, $CHCl_3$) but only slightly soluble in methanol.



Remarkably, 2-bromotoluene, which can be considered as the parent compound of 2-(2-bromophenyl)ethanol, reacts much less readily with $Pd(dba)_2$ under the same reaction conditions and affords only a 7% yield of the arylpalladium bromide complex 2.[15] Therefore, this compound is preferably prepared via oxidative addition of 2-iodotoluene to $Pd(dba)_2$ followed by consecutive anion exchange reactions with $AgNO_3$ and LiBr (eq 1b).

The ^1H NMR spectrum of 1 in $CDCl_3$ (200 MHz) shows the $ArCH_2$ protons as the A and M multiplets of an AMXY system. The CH_2OH groups appears as a triplet at 4.04 ppm, and the hydroxyl proton is present as a broad singlet at ca. 2.3 ppm. Four singlets are observed for the NCH_3 groups, whereas the NCH_2CH_2N protons appear as complex multiplets between 2.4 and 2.8 ppm. These observations are consistent with a perpendicular position (on the NMR time scale) of the aryl ring to the square coordination plane around Pd that renders both the $ArCH_2$ and the CH_2OH groups diastereotopic. The crystal structure of 1 (vide infra) confirms the perpendicular position of the aryl ring; i.e., the compound exists in two enantiomeric forms. No significant spectral changes are observed on heating the sample to 60 °C, which indicates that no racemization occurs on the NMR time scale.

When a solution of 1 in CD_3OD is heated, however, rapid inversion of the planar chirality around Pd occurs. This is indicated by the coalescence of two of the four NCH_3 group signals and the coalescence of the two signals of the $ArCH_3$ protons. At ~60 °C, the spectrum is consistent with the presence of an (apparent) plane of symmetry coinciding with the square coordination plane around Pd (Figure 1).

From the coalescence temperature of the two NCH_3 groups (28 °C) the overall free energy of activation ($\Delta G^\ddagger$) is calculated to be 14.9 kcal/mol.[16] The racemization can be envisioned as rapid rotation by 180° of the aryl ring around the Pd–C(ipso) bond. An alternative process that also results in coalescence and the formation of a plane of symmetry is dissociation of the Pd–Br bond to give the

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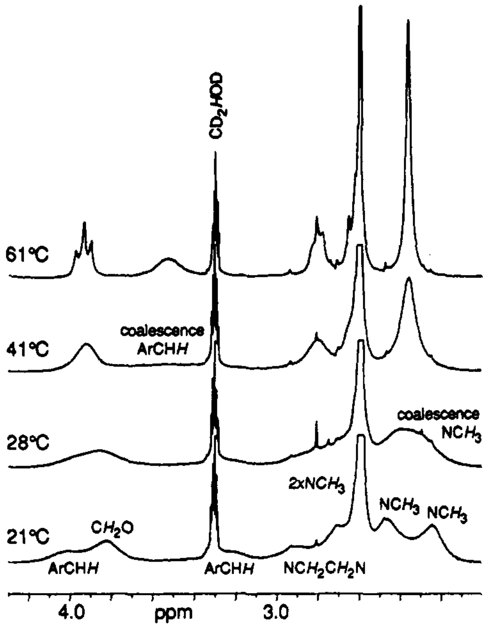


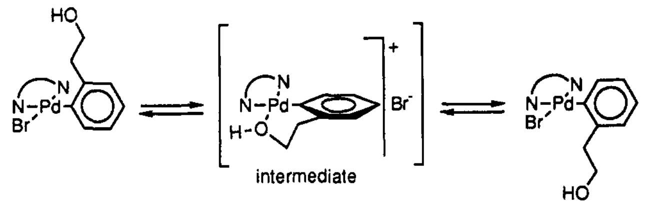
Figure 1. ^1H NMR spectra (200 MHz) of 1 in CD_3OD solution in the temperature range 21–61 °C.

cationic complex $[Pd\{C_6H_4(CH_2CH_2OH)\text{-}2\}(tmeda)]^+$, in which the alcohol functionality coordinates to the metal in a six-membered, conformationally nonrigid chelate ring. This latter possibility can be rejected, as the coalescence of both the $ArCH_2$ and NCH_3 resonances results in signals with a chemical shift at the mean position of the resonances before coalescence, which is only in agreement with the former process. Moreover, the spectrum of the cationic complex 3 formed upon treatment of 1 with $AgNO_3$ (vide infra) exhibits large differences from the spectrum of 1 at 60 °C in CD_3OD solution that are unlikely to be the result of differences in the nature of the anion (NMR data are presented in the Experimental Section).

To investigate whether the presence of a hydroxyl group in the side chain is a prerequisite for this rotation or whether the interconversion between the two enantiomers is simply thermally induced, the variable-temperature behavior of the methyl analogue $[PdBr\{C_6H_4Me\text{-}2\}(tmeda)]$ (2) was examined. When CD_3OD solutions of 2 were heated to ~60 °C, the ^1H NMR spectrum did not change significantly. No line broadening was observed, and the NCH_3 groups resonate as four sharp singlets over the whole temperature range. Thus, the perpendicular position of the aryl plane is maintained even at higher temperatures, and no interconversion between the two enantiomeric forms is observed on the NMR time scale. This indicates that the OH group is indeed necessary to induce rotation of the aryl ring in 1. This conclusion, combined with the observation that the fluxional behavior of 1 is only manifested in a polar, protic solvent such as methanol and not chloroform, is strong evidence that the rotation of the aryl ring is initiated by substitution of the hydroxyl group for the bromide anion in an intramolecular ionization, which is likely to be the rate-determining step (Scheme I).[17]

The concentrtaion of the resulting ionic intermediate, which can be isolated when nitrate instead of bromide is present as the counterion (vide infra), is too low to allow its identification by ^1H NMR at temperatures at which the bromide displacement occurs. Further evidence for the occurrence of Pd–Br bond ionization as the rate-determining step of the rotation process of the aryl ring is the observation that on addition of 3.2 equiv of $[PhCH_2NMe_3]Br$ to a solution of 1 in CD_3OD, the coalescence temperature of the two NCH_3 groups is raised by 23 °C.

Scheme I



Synthesis and Characterization of 3. Stoichiometric halide abstraction from neutral 1 with $AgNO_3$ (Scheme II) affords the yellow compound 3, which is very soluble in methanol and water but only slightly soluble in dichloromethane. The presence of nitrate was proved by the infrared spectrum.[18] The ^1H NMR spectra in D_2O, CD_3OD, or CD_2Cl_2 show four triplets for the CH_2 groups and two singlets for the NCH_3 groups. These spectra clearly indicate that the coordination plane around Pd is a plane of symmetry. Together, the spectral features and the solubility properties indicate that the compound is ionic, with the alcohol group coordinated to the metal in a C,O monoanionic chelate ring. In CD_2Cl_2 the OH proton is visible in the ^1H NMR spectrum as a broadened singlet at 9.1 ppm and this disappears upon addition of D_2O. The proposed structure is confirmed by a single-crystal X-ray analysis (vide infra).

Reaction of 3 with Bases. A 0.05 M solution of 3 in doubly distilled water is very weakly acidic (pH 6.2; $pK_a \approx 11$). Accordingly, 3 can be readily deprotonated with potassium methoxide. The resulting beige palladium alkoxide 4 is stable for months at room temperature as a solid but decomposes slowly in solution with formation of metallic palladium. Its ^1H NMR spectrum (CD_3OD) resembles that of the corresponding protonated derivative 3. When a CD_3OD solution of 3 is heated to 61 °C, there are no significant changes of the chemical shifts toward those found for the alkoxide 4, and this indicates that heating 3 does not lead to any significant increase in the concentration of the alkoxide. Both observations show that equilibrium 2 lies strongly to the left.

$$3 + ROH \rightleftharpoons 4 + ROH_2^+ + NO_3^- \qquad (2)$$

$$R = H, Me$$

Apparently, the oxygen atom of the alkoxide is much more negatively charged than that of water or methanol. The high negative charge of late-transition-metal alkoxides and phenoxides has recently been noted by several other authors, who found that even alcohols and phenols are acidic enough to form strong hydrogen bonds with the ligated oxygen atom.[7g,h,19]

Reaction of 3 with pyridine may a priori either lead to deprotonation to give the alkoxide 4 or effect a substitution of the coordinated hydroxyl group. When 1 equiv of pyridine is added to a CD_3OD solution of 3, the ^1H NMR

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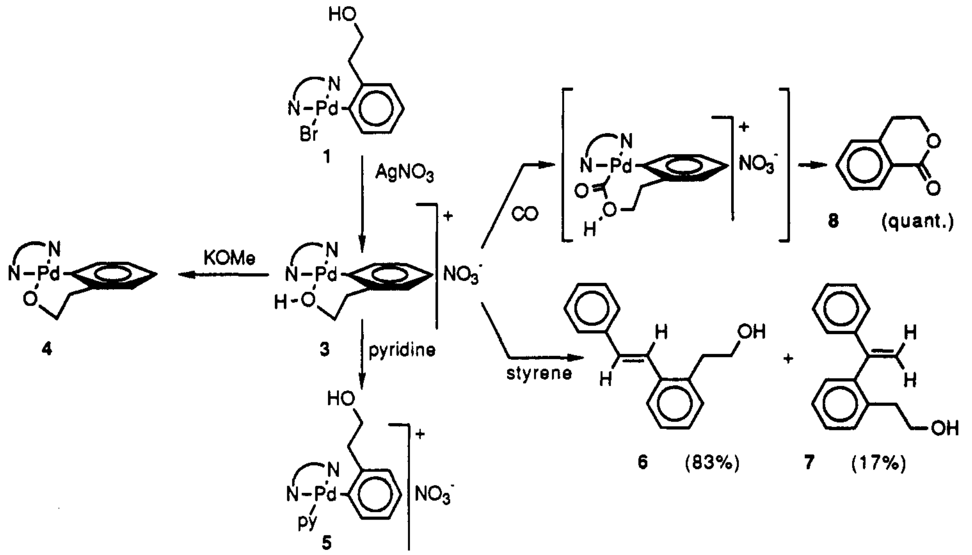
[17] See ref 14b for other evidence for the formation of chelate-stabilized cationic palladium alcohol complexes from the corresponding halide in solution.

[18] Hathaway, B. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D.; McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; p 420.

Scheme II



spectrum of this solution shows four different singlets for the NCH_3 groups and complex multiplets for the CH_2 groups. Signals attributable to 4 are absent. Clearly, the product is devoid of symmetry, consistent with formation of the cationic pyridine adduct 5 rather than the alkoxide 4.

Reactivity of 3 toward Styrene and Carbon Monoxide. The reaction of 3 with excess styrene results in the quantitative formation (based on Pd) of three isomeric products (GC–MS analysis) with concomitant formation of metallic palladium. Two of the products (in the ratio 5:1) could be separated by HPLC. The third product is formed in trace amounts and was not isolated pure. The main product was identified as the stilbene derivative 6, which has the trans configuration based on the large vicinal trans coupling (16 Hz) observed for the olefinic protons and shows a broad O*H* resonance at 1.66 ppm. The ^1H NMR spectrum of the second product 7 is consistent with that of a geminally disubstituted alkene because of the very small coupling (1.3 Hz) of the two geminal olefinic protons at 5.78 and 5.20 ppm; the chemical shift of the olefinic protons is typical for a 1,1-diaryl-substituted ethene. A broad resonance at 1.55 ppm points to the presence of an alcoholic OH group. The above and other spectroscopic features are consistent with the formulation of 7 as a 1,1-diaryl-substituted ethene.[20] A geminally disubstituted alkene may also be formed by a charge-controlled trans attack of the liberated hydroxyl group at the coordinated styrene, which would lead to the formation of a geminally disubstituted vinyl ether.[6a] Such a behavior can be expected for hard nucleophiles such as a OH group.[21] However, this process can be safely rejected, as the olefinic protons in 1-phenyl-1-alkoxyethenes resonate at much higher field (e.g. 4.67 and 4.16 ppm for $(Ph)(EtO)C{=}CH_2$)[22] than those of 1,1-diarylethenes, and moreover, no O*H* resonance would be visible for such a vinyl ether. The mass spectrum of the third trace product is almost identical with that of the main product. Therefore, this product is very likely to be the *cis*-stilbene derivative. Interestingly, the deprotonated form of 3, i.e. the alkoxide 4, was found to be unreactive toward styrene, and this points to a much greater lability of a coordinated alcohol functionality in 3 compared to the corresponding alkoxy group in 4.

Complex 3 also reacts rapidly in quantitative yield with carbon monoxide to afford the lactone dihydroisocoumarin (8). This product may be formed either via initial CO insertion into the Pd–aryl bond or via insertion of CO into the Pd–O bond. Recent work of Yamamoto et al. shows that methylpalladium alkoxides preferentially release carboxylic esters upon reaction with carbon monoxide via insertion in the Pd–alkoxide bond rather than in the Pd–methyl bond.[7d,h] As the Pd–O bond of the coordinated alcohol in 3 is certainly more labile than the Pd–aryl bond, we assume that also in our case reductive elimination of the lactone proceeds via a (protonated) alkoxycarbonyl intermediate rather than via an acyl complex.[23]

Molecular Structures of 1 and 3. The molecular structure of 1 (Figure 2) shows a slightly distorted square-planar coordination around palladium. Bond distances and bond angles are collected in Table I.

The aryl ring is nearly perpendicular to the coordination plane. The Pd–N(1) and Pd–C(1) bond distances are almost identical with those observed in the closely related compound [PdIPh(tmeda)],[24] whereas the Pd–N(2) bond is slightly shorter. The long Pd–N(1) bond length (2.190(6) Å) is typical for an amine trans to a σ-bonded carbon ligand. The hydroxyl group is intramolecularly hydrogen bonded to the bromide ligand (Br- - -H–O = 168(7)°). As the Br- - -O distance (3.361(5) Å) is almost equal to the sum of the van der Waals radii,[25] the interaction is weak

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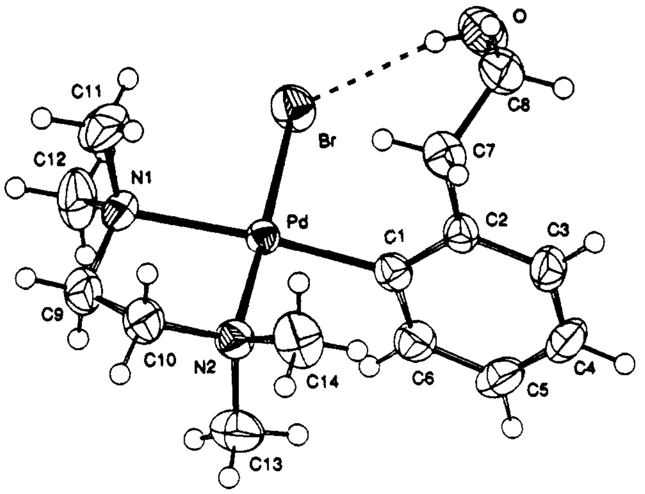

Figure 2. ORTEP drawing (50% probability level) of the molecular structure of [PdBr{$C_6H_4(CH_2CH_2OH)$-2}(tmeda)] (1) together with the adopted numbering scheme.

and probably better described as a dipole–dipole interaction. The chemical shift of the O*H* proton (ca. 2.3 ppm in $CDCl_3$; cf. δ(O*H*) 2.48 ppm for 2-(2-bromophenyl)-ethanol) suggests that in solution hydrogen bonding is only of minor importance. Nevertheless, in the solid phase it is strong enough to force the ethanol skeleton to adopt approximately the energetically least favored[26] eclipsed cis conformation. As a result, the C(7)–C(8)–O angle opens up to 114.1(5)°.[27] The possibility of hydrogen bonding between alcohols and halide ligands of platinum(II) complexes has been deduced from the kinetics of ligand substitution reactions in alcoholic solvents,[28] and the present structure provides further proof for this.

The molecular structure of **3** (Figure 3) shows the complex to be ionic, with a metal-centered cation and a nitrate anion. Compared to **1**, the palladium has a hydroxyl group of the $ArCH_2CH_2OH$ ligand replacing the bromine atom.

The palladium center has a slightly distorted square-planar coordination. The aryl ring is part of a six-membered chelate ring, which has a boat conformation, and is strongly tilted with respect to the square plane around Pd, the torsion angle C(2)–C(1)–Pd–O(1) being 41.7(6)°. The Pd–C(1) and Pd–N(2) bond distances are similar to the corresponding bond lengths found in **1**. The Pd–N(2) bond length is, however, significantly shorter than the Pd–N bond trans to the bromide in **1**, which reflects the weaker trans influence of the coordinated OH group than that of a bromide ligand. As no crystal structures of monomeric palladium alkoxides[29] or palladium alcohol complexes are known, it is hard to evaluate the Pd–O(1) bond length of 2.076(4) Å. It is useful to compare it with the Pd–C bond length of 2.03 Å in the dimethyl compound $[PdMe_2(tmeda)]$.[30] From the difference in bond length between single $C(sp^3)$–$C(sp^3)$ bonds (ca. 1.54 Å) and $C(sp^3)$–$O(sp^3)$ bonds (ca. 1.42 Å), a length of approximately 1.91 Å might be expected for a Pd–alkoxide bond trans to a tertiary amine ligand.[31] A comparison of this value with the observed Pd–O bond length of 2.071(4) Å in the protonated alkoxide **2** suggests that protonation of the oxygen atom greatly lengthens the Pd–O bond by 0.16 Å.[32]

The hydroxyl group is hydrogen-bonded to the nitrate group. The O(1)- - -O(3) distance of 2.669(5) Å is somewhat longer than the values found for hydrogen-bonded phenols and alcohols.[33] The O(1)- - -O(4) distance of 3.144(6) Å is too long to indicate a significant interaction, and therefore, the hydrogen bond is probably not bifurcated. As expected, the bridging hydrogen is closer to the alkoxide oxygen atom than to the nitrate group.

Comparison of the Structural Features of 1 and 3 with Those of Late-Transition-Metal Alkoxides. An interesting structural aspect of late-transition-metal alkoxides and phenoxides is the presence of C–O bonds that are shorter than the C–O bond length in analogous organic compounds, with the O–CH_3 bond length (1.258(19) Å) in the complex [PtMe(OMe)(dppe)] approaching that of a double bond being an extreme case.[2] The C–O bond lengths in platinum and iridium methoxides, which are typically 1.33–1.37 Å,[1] are significantly shorter than the C–O length of ca. 1.41 Å normally found in alkoxides[34] and the length of ca. 1.43 Å found in alcohols.[35] So far, no satisfying explanation has been offered for this C–O bond shortening, although it has been suggested that it reflects the tendency of late-transition-metal alkoxides to decompose via β-elimination.[36] However, the fact that the C–O distances in $[Pt(OMe)_2(dppe)]$ are virtually identical, whereas only one OMe group has a position with respect to the square plane that allows β-hydride elimination,[2] makes this explanation unlikely. In our opinion, the C–O bond shortening is better explained by a recent model developed by Wiberg based on ab initio calculations on alkoxides and alkoxide anions.[37]

Wiberg showed that the negatively charged oxygen atom in an alkoxide anion repels charge from the carbon atom of the adjacent CH_3 (or CH_2R) group onto the groups attached to this carbon atom. This results in an attractive Coulombic interaction between carbon and oxygen, thus shortening the C–O bond. This stabilization is largest

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[26] Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2371.

[27] For some calculations on the dependence of tilt angles on molecular conformation, see: (a) Pross, A.; Radom, L.; Riggs, N. V. *J. Am. Chem. Soc.* **1980**, *102*, 2253. (b) van Alsenoy, C.; Scarsdale, J. N.; Williams, J. O.; Schäfer, L. *J. Mol. Struct.* **1982**, *86*, 365. (c) Ohsaku, M.; Ichiishi, T.; Imamura, A.; Hayashi, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2791. For a spectroscopic measurement, see: Sasada, Y.; Takano, M.; Satoh, T. *J. Mol. Spectrosc.* **1971**, *38*, 33.

[28] Krylova, L. F.; Luk'yanova, I. G.; Zelenkov, V. N. *Zh. Neorg. Khim.* **1979**, *24*, 1615.

[29] Several crystal structures of much more electronegative fluorinated palladium alkoxides are known (for some references, see: Willis, C. J. *Coord. Chem. Rev.* **1988**, *88*, 133).

[30] de Graaf, W.; Boersma, J.; Grove, D. M.; Spek, A. L.; Smeets, W. J. J.; van Koten, G. *Organometallics* **1989**, *8*, 2907.

[31] This reasoning holds for platinum alkoxides.[36]

[32] We have recently prepared the palladium bis(alkoxide) derived from *N*-methyldiethanolamine, i.e. the complex *trans*-$[Pd\{OCH_2CH_2N(Me)CH_2CH_2OH\}_2]$. Its structure was established by X-ray diffraction. The trans structure suggests that the trans influence of an alkoxide donor is approximately equal to that of a tertiary amine donor. The Pd–O distance in this compound is 2.002(3) Å, which is longer than the value of 1.91 Å calculated by comparison with $[Pd(Me)_2(tmeda)]$. Therefore, the calculated lengthening of the Pd–O bond upon protonation at oxygen (0.16 Å) may be greatly exaggerated. Other relevant geometrical parameters are as follows: Pd–O–C = 109.4(2)°; C–OPd = 1.403(5) Å; C–OH = 1.409(6) Å.

[33] An overview of O- - -O distances in hydrogen-bonded late-transition-metal species can be found in ref 19e.

[34] Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: London, 1978.

[35] Sutton, L. E., Ed. *Tables of Interatomic Distances and Configuration in Molecules and Ions*; The Chemical Society: London, 1965; Special Publication 18.

[36] Alcock, N. W.; Platt, A. W. G.; Pringle, P. *J. Chem. Soc., Dalton Trans.* **1987**, 2273.

[37] (a) Wiberg, K. B. *J. Am. Chem. Soc.* **1990**, *112*, 3379. (b) Wiberg, K. B.; Breneman, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 8765.

Table I. Selected Interatomic Distances (Å) and Angles (deg) for [PdBr{$C_6H_4(CH_2CH_2OH)$-2}(tmeda)] (1) and [Pd{$C_6H_4(CH_2CH_2OH)$-2}(tmeda)]NO_3 (3)

	1	3		1	3
		Distances			
Pd–C(1)	1.990(7)	1.976(4)	O–C(8)	1.412(8)	1.448(7)
Pd–Br	2.4315(7)		O–H	0.83(8)	0.73(6)
Pd–O		2.076(4)	Br- - -O	3.361(5)	
Pd–N(1)	2.190(6)	2.191(4)	O- - -O(2)		2.669(5)
Pd–N(2)	2.118(4)	2.071(4)	C(7)–C(8)	1.534(8)	1.505(7)
C(9)–C(10)	1.524(9)	1.456(8)	C(2)–C(7)	1.508(9)	1.507(8)
N(1)–C(9)	1.483(8)	1.481(6)	N(2)–C(10)	1.491(8)	1.544(8)
N(1)–C(11)	1.495(10)	1.459(12)	N(2)–C(13)	1.497(8)	1.472(13)
N(1)–C(12)	1.477(9)	1.472(12)	N(2)–C(14)	1.478(8)	1.430(13)
av C–C(aryl)	1.390	1.396			
		Angles			
C(1)–Pd–Br	89.96(16)		Pd–O–C(8)		122.7(3)
C(1)–Pd–O		87.8(2)	O–C(8)–C(7)	114.1(5)	109.0(4)
C(1)–Pd–N(2)	92.3(2)	96.06(18)	C(8)–C(7)–C(2)	113.1(5)	111.3(5)
Br–Pd–N(1)	93.89(14)		C(1)–C(2)–C(7)	122.4(6)	119.1(5)
O–Pd–N(1)		91.46(17)	C(3)–C(2)–C(7)	118.9(5)	120.3(5)
N(1)–Pd–N(2)	84.1(2)	84.96(15)	C(2)–C(1)–C(6)	118.1(6)	117.9(4)
C(1)–Pd–N(1)	174.8(2)	177.9(4)	av C–C–C(aryl)	120.0	120.0
Br–Pd–N(2)	175.05(14)		Br- -H–O	168(7)	
O–Pd–N(2)		169.8(3)	O–H- -O(2)		156(9)
Pd–N(1)–C(9)	104.5(4)	104.0(3)	Pd–N(2)–C(10)	106.0(3)	102.4(3)
Pd–N(1)–C(11)	110.3(5)	112.3(5)	Pd–N(2)–C(13)	112.0(4)	110.4(6)
Pd–N(1)–C(12)	113.8(5)	109.7(5)	Pd–N(2)–C(14)	112.6(4)	118.1(6)
N(1)–C(9)–C(10)	109.9(5)	111.5(5)	N(2)–C(10)–C(9)	110.4(5)	109.5(5)
		Torsion Angles			
C(6)–C(1)–Pd–N(2)	82.8(5)	58.4(7)			
H–O–C(8)–C(7)	20(6)	176(6)			
Pd–O–C(8)–C(7)		–4.2(5)			

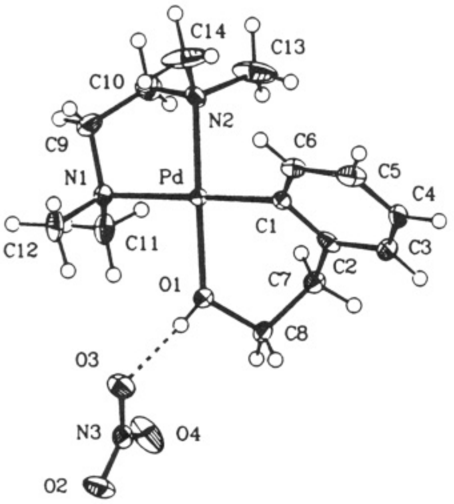

Figure 3. ORTEP drawing (50% probability level) of the molecular structure of [Pd{$C_6H_4(CH_2CH_2OH)$-2}(tmeda)]NO_3 (**3**) together with the adopted numbering scheme.

(and the C–O bond is shortest) when the lone pairs are antiperiplanar to a C–H bond,[38] because only this position allows an "interaction between a lone pair and the backside of a C–H bond", as Wiberg puts it. Such an increase in the H_3C–X (X = CH_3, NH_2, OH) bond length upon rotation from a staggered to an eclipsed conformation is calculated to be a general feature for ethane, methylamine, or methanol, although for the latter the increase in C–O bond length is very small.[39]

This theoretical result may explain why the C–O bond shrinkage has been observed for late-transition-metal methoxides but not for compounds in which the alkoxide is part of a five-membered chelate ring.[36,40] The effect of chelation on the C–O bond length can be studied by comparing the crystal structures of [Pt$(OMe)_2$(dppe)] (C–O = 1.370(14) Å)[2] and [Pt$(OCH_2CH_2PPh_2)_2$] (C–O = 1.413(10) Å),[40] which both have an otherwise very similar set of ligands around platinum. The interaction of the oxygen lone pairs with the backsides of the C–H bond orbitals is less efficient in the latter case, as the C–H bonds are partly turned toward an eclipsed position with respect to the lone pairs due to the rather flat geometry of the chelate ring (Figure 4).[41] The methyl group of a methoxide ligand is free to adopt a staggered position, which allows C–O bond shortening via backside interaction. The observed qualitative dependence of the C–O bond length on the conformation of the (late transition) metal alkoxide (staggered or eclipsed) is thus the same for both the alcohol

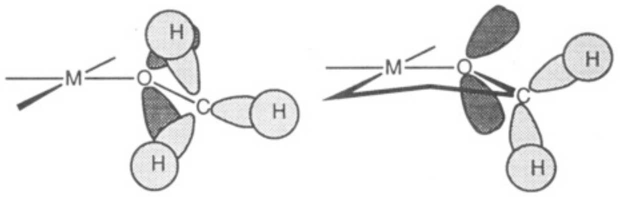

Figure 4. Rotation of C–H bonds toward an eclipsed position with respect to the lone pairs on the oxygen atom of an alkoxide ligand that is part of a five-membered chelate ring (right) compared to the staggered conformation adopted in a methoxide group (left).

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[38] Wiberg showed this by calculating inter alia the variation of the backside interaction with the conformation of methanol, being largest in the staggered conformation and smallest in the eclipsed conformation.

[39] Bader, R. F. W.; Cheeseman, J. R.; Laidig, K. E.; Wiberg, K. B.; Breneman, C. *J. Am. Chem. Soc.* **1990**, *112*, 6530.

[40] Alcock, N. W.; Platt, A. W. G.; Pringle, P. *J. Chem. Soc., Dalton Trans.* **1989**, 139.

[41] The M–O–C angle in late-transition-metal alkoxides ranges from 109 to 120°. These values suggest that the hybridization of the oxygen atom ranges from sp^3 to sp^2. In the latter case, two equivalent sp^5 hybrid lone-pair orbitals can be constructed from the lone-pair p and lone-pair sp^2 orbital. The angle between two sp^5 orbitals is ca. 102°, which is slightly smaller than the H–C–H angle of 109° between the adjacent C–H bonds (see Figure 4).

and the corresponding metal alkoxide, but in metal alkoxides the effect is more pronounced, as the backside interaction is stronger due to the higher negative charge on oxygen.[42]

As a result of partial electron donation to the metal, the C–O bond in the alcohol adduct **3** (1.448(7) Å) is significantly longer than the C–OH bond of the free alcohol in **1** (C–O = 1.412(8) Å). The modest lengthening of the C–O bond on coordination to palladium (0.036 Å) in **3** compared to the calculated increase in bond length on protonation (ca. 0.11 Å for $MeOH \rightarrow MeOH_2^+$)[43] suggests that the electron density in the Pd–O bond is still concentrated on the oxygen atom and that the ROH group is only weakly coordinated to the metal.[44] This argumentation is in line with the long Pd–O bond length and the shortened trans Pd–N(1) bond.

According to this discussion, short C–O bonds are an intrinsic property of alkoxide ligands (provided that backside interaction is possible and that the oxygen atom carries a high negative charge) and they do not reflect the tendency of late-transition-metal alkoxides to decompose via β-hydride abstraction. However, the adopted explanation cannot fully account for the extremely short C–O bond length in [PtMe(OMe)(dppe)], which, even though the complex is quite resistant toward β-elimination, is much shorter than that of a free methoxide anion.[2] This complex seems exceptional when compared with the limited number of other late-transition-metal alkoxides whose structures have been solved by X-ray diffraction. A detailed theoretical calculation may reveal the reason for the extreme bond shortening in this compound.

Conclusions

It has been shown that the presence of an alcohol function in the side chain of the ortho-substituted (planar)-chiral arylpalladium bromide **1** facilitates rotation of the aryl ring around the Pd–C bond in polar protic solvents such as methanol. This rotation operates via initial substitution of the hydroxyl group for the bromide ligand.

Incorporation of the oxygen atom in a six-membered chelate ring allows the preparation of stable organopalladium complexes containing a coordinated alcohol group (**3**) or alkoxide ligand (**4**). The kinetic lability of the Pd–O bond in **3** is expressed by the rapid substitution of pyridine for the coordinated hydroxyl group and by the high reactivity of **3** toward styrene and carbon monoxide.

Finally, it is shown that late-transition-metal alkoxides seem to behave qualitatively in the same way as the corresponding alcohols with respect to the dependence of the C–O bond length on the conformation (position of the oxygen lone pairs) of the alkoxide group, but more structural information concerning these compounds is needed to fully assess the validity of this statement. The concept of backside interaction of lone pairs on oxygen and antiperiplanar C–H bonds as proposed by Wiberg[37] is very useful to understand at least part of the observed C–O bond shortening (compared to alcohols) in late-transition-metal alkoxides. The C–O bond shortening in these compounds is of the same order of magnitude (though generally smaller) than is theoretically predicted for alkoxide anions. This is a result of their monomeric nature combined with a high negative charge on the oxygen atom due to the absence of π-interaction with the metal, a combination that is rarely fulfilled in alkoxide chemistry. Accordingly, the C–O bond shortening does not reflect the tendency of late-transition-metal alkoxides to decompose via β-elimination.

Experimental Section

General Considerations. Reactions performed under an atmosphere of nitrogen were carried out using standard Schlenk techniques. C_6H_6, Et_2O, and pentane were freshly distilled from sodium–benzophenone ketyl. CH_2Cl_2 was distilled from calcium hydride. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 spectrometer. The GC–MS analyses were carried out at the Analytical Chemical Laboratory of the University of Utrecht. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. HPLC separations were carried out on a Philips PU 4100 liquid chromatograph system with a Supelco reversed-phase LC-18 column. Elemental analyses were carried out by the Institute of Applied Chemistry (TNO), Zeist, The Netherlands, or by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. The starting materials $Pd(dba)_2$[45] and 2-(2-bromophenyl)ethanol[46] were prepared according to literature procedures. Abbreviations: dt = doublet of triplets, td = triplet of doublets.

2-(2-Bromophenyl)ethanol ^1H NMR ($CDCl_3$, δ): 7.52 (d, 1H, ^3J = 8 Hz, Ar*H* (ortho)); 7.22 (m, 3H, Ar*H*); 7.05 (m, 1H, Ar*H*); 3.81 (t, 2H, ^3J = 7 Hz, CH_2OH); 2.98 (t, 2H, ^3J = 7 Hz, $ArCH_2$); 2.48 (s, 1H, O*H*).

Synthesis of [PdBr{$C_6H_4(CH_2CH_2OH)$-2}(tmeda)] (1). To a solution of $Pd(dba)_2$ (5.86 g; 10.2 mmol) in freshly distilled C_6H_6 (250 mL) was added a mixture of 2-(2-bromophenyl)ethanol (11.03 g; 54.9 mmol) and tmeda (2.56 g; 22.0 mmol) in C_6H_6 (10 mL) under a nitrogen atmosphere. The very dark purple-brown mixture was stirred for 18 h under nitrogen at a bath temperature of 65–70 °C. Metallic palladium was filtered off, and the yellow filtrate was concentrated in vacuo. The remaining syrup was triturated with pentane (100 mL), and the resulting orange-yellow solid was filtered off. The solid was washed extensively with pentane (2 × 100 mL) and Et_2O (6 × 75 mL) until the filtrate was colorless. Finally, the slightly yellow-orange powder was washed once with pentane (75 mL) and dried in vacuo: yield 2.50 g (58%). Crystals suitable for X-ray diffraction were obtained by diffusion of Et_2O into an acetone solution of **1**. Mp: 156 °C dec. ^1H NMR ($CDCl_3$; δ): 7.22 (m, 1H, ortho *H*); 6.76–6.90 (m, 3H, Ar*H*); 4.04 (t, 2H, ^3J = 6 Hz, CH_2O); 3.87 (dt, 1H, ^2J = 13 Hz, ^3J = 6 Hz, ArC*H*H); 3.18 (dt, 1H, ^2J = 13 Hz, ^3J = 6 Hz, ArCH*H*); 2.43–2.87 (m, 4H, NCH_2CH_2N); 2.34 (bs, 1H, O*H*); 2.17, 2.43, 2.59, 2.60 (s, 3H, NCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 148.04, 141.95, 134.96, 127.53, 124.75, 123.21 (Ar); 63.69, 62.66 (NCH_2; CH_2O); 58.15 (CH_2N); 51.25, 49.72, 49.03, 47.73 (NCH_3); 42.01 ($ArCH_2$). Anal. Calcd: C, 39.69; H, 5.96; N, 6.61. Found: C, 39.16; H, 5.89; N, 6.65.

Synthesis of [PdBr{C_6H_4Me-2}(tmeda)] (2). $PdI(C_6H_4Me$-2)(tmeda) was prepared in a way analogous to that recently described for $PdI(C_6H_5)$(tmeda),[19] by starting from *o*-tolyl iodide. This was converted to the bromide complex by first removing the iodide with a slight excess of $AgNO_3$ in MeOH, followed by addition of a 10-fold excess of LiBr. After the MeOH was removed under reduced pressure, the solid residue was extracted with CH_2Cl_2. Evaporation of the solvent afforded **2** in quantitative

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[42] Kirby et al. have shown that the exocyclic C–OR bond length in tetrahydropyranyl acetals can decrease ca. 0.03 Å on changing from an axial to an equatorial position, which shows that the C–O bond length is subject to stereoelectronic effects: Briggs, A. J.; Glenn, R.; Jones, P. G.; Kirby, A. J.; Ramaswamy, P. *J. Am. Chem. Soc.* **1984**, *106*, 6200.

[43] (a) Del Bene, J. E.; Frisch, M. J.; Raghavachari, K.; Pople, J. A. *J. Phys. Chem.* **1982**, *86*, 1529. (b) Hopkinson, A. C.; Lien, M. H. *J. Mol. Struct.* **1983**, *92*, 153. (c) Grein, F. *Can. J. Chem.* **1985**, *63*, 1988.

[44] Not only protonation but also bridging between two palladium centers causes a large increase in the C–O bond length of the alkoxide. Siedle, A. R.; Pignolet, L. H. *Inorg. Chem.* **1982**, *21*, 3090.

[45] Rettig, M. F.; Maitlis, P. M.; Cotton, F. A.; Webbs, T. R. *Inorg. Synth.* 1971, 134.

[46] Bickelhaupt, F.; Stach, K.; Thiel, M. *Chem. Ber.* **1965**, *98*, 685.

yield as a yellow solid, which was recrystallized by diffusion of Et_2O into a solution of **2** in CH_2Cl_2. ^1H NMR ($CDCl_3$; δ): 7.18 (m, 1H, ortho *H*); 6.74–6.82 (m, 3H, Ar*H*); 2.14–2.85 (m, 4H, NCH_2CH_2N); 2.77, 2.63, 2.62, 2.52 (s, 3H, NCH_3); 2.23 (s, 3H, $ArCH_3$); ^1H NMR (CD_3OD; δ): 7.11–7.15 (m, 1H, ortho *H*); 6.66–6.80 (m, 3H, Ar*H*); 2.48–3.05 (m, 4H, NCH_2CH_2N); 2.74, 2.60, 2.57, 2.52 (s, 3H, NCH_3); 2.21 (s, 3H, $ArCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 147.71, 141.42, 134.18, 127.96, 123.80, 122.83 (Ar); 62.61, 58.13 (NCH_2CH_2N); 51.10, 49.38, 49.00, 47.47 (NCH_3); 25.98 ($ArCH_3$). Anal. Calcd: C, 39.66; H, 5.89; N, 7.12. Found: C, 40.30; H, 5.87; N, 7.14.

Synthesis of $[Pd\{C_6H_4(CH_2CH_2OH)\text{-}2\}(tmeda)]NO_3$ (3). A mixture of **1** (2.27 g; 5.36 mmol) and $AgNO_3$ (0.94 g; 5.53 mmol) in MeOH (150 mL) was stirred for 3 h in the dark. The mixture was filtered, and the filtrate was evaporated to dryness in vacuo. The solid residue was taken up in CH_2Cl_2 (600 mL), and the solution was filtered over Celite. The solvent was removed under reduced pressure. The remaining yellow solid was washed with Et_2O (4 × 20 mL) and pentane (4 × 20 mL) and dried: yield 2.00 g (92%). Large yellow needles suitable for X-ray diffraction were obtained by diffusion of Et_2O into a MeOH solution of **3**. Mp: 130 °C dec. ^1H NMR (D_2O; δ): 7.33 (m, 1H, ortho *H*); 6.95–7.00 (m, 3H, Ar*H*); 3.72 (t, 2H, ^3J = 6 Hz, CH_2O); 3.48 (t, 2H, ^3J = 6 Hz, $ArCH_2$); 2.84, 2.64 (t, 2H, ^3J = 6 Hz, NCH_2); 2.53, 2.52 (s, 6H, $N(CH_3)_2$). ^1H NMR (CD_3OD; δ): 7.24 (m, 1H, ortho *H*); 6.90–7.00 (m, 3H, Ar*H*); 3.48 (t, 2H, ^3J = 5 Hz, CH_2O); 3.41 (t, 2H, ^3J = 5 Hz, $ArCH_2$); 2.94, 2.69 (t, 2H, ^3J = 6 Hz, NCH_2); 2.69, 2.61 (s, 6H, $N(CH_3)_2$). ^1H NMR (CD_2Cl_2; δ): 9.1 (bs, 1H, O*H*); 7.16 (m, 1H, ortho *H*); 6.85–7.02 (m, 3H, Ar*H*); 3.52 (bt, 2H, CH_2O); 3.25 (t, 2H, ^3J = 5 Hz, $ArCH_2$); 2.78, 2.57 (t, 2H, ^3J = 5 Hz, NCH_2); 2.63, 2.61 (s, 6H, $N(CH_3)_2$). $^{13}C\{^1H\}$ NMR (D_2O; δ): 150.42, 144.02, 135.90, 129.45, 127.73, 127.33 (Ar); 66.56, 64.45 (NCH_2); 59.58 (CH_2O); 53.80, 49.04 ($N(CH_3)_2$); 42.95 ($ArCH_2$). IR (KBr; ν, cm^{-1}): 2500–3000 (vb, O–H- - -O); 1470, 1380, 1300 (vs, NO_3). Anal. Calcd: C, 41.43; H, 6.22; N, 10.36; O, 15.77. Found: C, 41.20; H, 6.11; N, 10.34; O, 15.38.

Synthesis of $[Pd\{C_6H_4(CH_2CH_2O)\text{-}2\}(tmeda)]$ (4). To a solution of **3** (0.60 g; 1.48 mmol) in MeOH (15 mL) was added KOMe (0.11 g; 1.57 mmol), dissolved in MeOH (4 mL). After 5 min the cloudy suspension was evaporated to dryness and the residue was taken up in CH_2Cl_2 (50 mL). The mixture was filtered over Celite, and the solvent of the clear yellow filtrate was removed in vacuo. The remaining solid was washed with pentane (3 × 30 mL) and dried: yield 0.50 g (97% for $PdC_{14}H_{24}N_2O\cdot 0.25H_2O$) of a beige powder. All efforts to crystallize the compound failed. The compound decomposes slowly in solution. Elemental analyses of different batches gave rise to low values for carbon, presumably because of the presence of water in the crystal lattice. Mp: 120 °C dec. ^1H NMR (CD_3OD; δ): 7.24–7.28 (m, 1H, ortho *H*); 6.76–6.86 (m, 3H, Ar*H*); 3.19 (merged triplets, 4H, CH_2O and $ArCH_2$); 2.77, 2.58 (t, 2H, ^3J = 5 Hz, NCH_2); 2.58, 2.56 (s, 6H, $N(CH_3)_2$). Anal. Calcd for $PdC_{14}H_{24}N_2O\cdot 0.25H_2O$: C, 48.42; H, 7.13; N, 8.07. Found: C, 47.88; H, 6.97; N, 7.95.

Reaction of 3 with Pyridine. To an accurately weighed amount of pyridine (0.0125 g; 0.158 mmol) was added **3** (0.0628 g; 0.158 mmol). The mixture was dissolved in CD_3OD (0.5 mL) to give a very pale yellow solution. The ^1H NMR spectrum showed the absence of **4** in the mixture and was consistent with the formation of the cationic coordination adduct **5**. The compound can be isolated as colorless crystals by diffusion of Et_2O into a solution of **5** in MeOH. ^1H NMR (CD_3OD; δ): 8.92 (dt, 2H, ^3J = 8 Hz, *J* = 1.6 Hz, ortho *H* py); 7.89 (tt, 1H, ^3J = 8 Hz, ^4J = 1.6 Hz, para *H* py); 7.55 (d, 1H, ^3J = 7 Hz, ortho *H*); 7.48 (tt, 2H, ^3J = 8 Hz, ^4J = 1.4 Hz, meta *H* py); 6.80–6.95 (m, 3H, Ar*H*); 3.65–3.81 (m, 2H, CH_2O); 3.46–3.58 (m, 2H, $ArCH_2$); 2.65–3.15 (m, 4H, NCH_2CH_2N); 2.58, 2.56, 2.40, 2.24 (s, 3H, NCH_3). $^{13}C\{^1H\}$ NMR (CD_3OD; δ): 153.37 (ortho *C* py); 152.93 (*C*–Pd); 142.97 ($ArCH_2$); 140.39 (para *C* py); 134.63, 128.23, 126.59, 125.16 (Ar); 127.43 (meta *C* py); 64.13, 63.95 (NCH_2CH_2N); 59.47 (OCH_2); 42.69 ($ArCH_2$); 52.34, 48.72, 49.00, 47.19 (NCH_3).

Reactivity of 3 toward Styrene. To a solution of **3** (0.41 g; 1.01 mmol) in freshly distilled CH_2Cl_2 (30 mL) under nitrogen was added styrene (0.33 g; 3.17 mmol), which was purified by passage through a short column of active alumina (neutral) before use. Within several minutes, the yellow solution turned into a black suspension. The mixture was stirred for 20 h under a nitrogen atmosphere, and metallic palladium was removed by filtration over Celite. The orange filtrate was evaporated under reduced pressure (1 mm at 60 °C for 1 h to remove the excess styrene), and the residue was extracted with pentane (4 × 15 mL) and Et_2O (3 × 15 mL). Evaporation of the solvents of the combined extracts gave 0.21 g of a slightly yellow syrup. According to a GC–MS analysis, this consisted of three isomers (total yield quantitative) in a ratio of 5:1:trace which could be separated by HPLC (eluent 70/30 MeOH/water). Main product (*trans*-stilbene **6**): ^1H NMR ($CDCl_3$; δ) 7.20–7.66 (m, 10H, Ar*H* + olefinic *H*), 7.01 (d, 1H, $^3J_{trans}$ = 16 Hz, olefinic *H*), 3.84 (t, 2H, ^3J = 7 Hz, CH_2O), 3.04 (t, 2H, ^3J = 7 Hz, $ArCH_2$), 1.66 (bs, 1H, O*H*); MS (*m/z* (relative intensity)) 224 (85, $M^{+\bullet}$), 206 (25, $M^{+\bullet} - H_2O$), 193 (26), 178 (54), 165 (17), 133 (93), 115 (100), 105 (51), 91 (70). Second product (1,1-diarylethene **7**): ^1H NMR ($CDCl_3$; δ): 7.21–7.32 (m, 10H, Ar*H*), 5.78 (d, 1H, $^2J_{gem}$ = 1.3 Hz, olefinic *H*), 5.20 (d, 1H, $^2J_{gem}$ = 1.3 Hz, olefinic *H*), 3.63 (t, 2H, ^3J = 7 Hz, CH_2O), 2.65 (t, 2H, ^3J = 7 Hz, $ArCH_2$); MS (*m/z* (relative intensity)) 224 (34, $M^{+\bullet}$), 206 (76, $M^{+\bullet} - H_2O$), 191 (60), 178 (100), 165 (30), 152 (11), 131 (24), 115 (60), 103 (21), 91 (31). Apart from these two products, a trace amount of a third product was formed, which was not isolated. As the mass spectrum is almost identical with that of the main product **6**, this component is very likely the *cis*-stilbene isomer: MS (*m/z* (relative intensity)) 224 (54, $M^{+\bullet}$), 206 (21, $M^{+\bullet} - H_2O$), 193 (25), 178 (56), 165 (21), 133 (80), 115 (100), 105 (52), 91 (64).

Reactivity of 3 toward Carbon Monoxide. Carbon monoxide was passed through a solution of **3** (0.31 g; 0.76 mmol) in CH_2Cl_2 (40 mL) for 20 min. The black suspension was filtered over Celite, and the solvent was removed from the yellow filtrate under reduced pressure. The orange-yellow residue was extracted with pentane (5 × 10 mL). After evaporation of the pentane from the combined extracts, 0.11 g of a colorless oil remained, which was identified by means of ^1H NMR, GC–MS, and IR as the lactone **8** (quantitative yield). ^1H NMR ($CDCl_3$; δ): 8.00, 7.20 (dd, 1H, ^3J = 8 Hz, ^4J = 1.3 Hz, Ar*H*), 7.47, 7.31 (td, 1H, ^3J = 8 Hz, ^4J = 1.5 Hz, Ar*H*), 4.46 (t, 2H, ^3J = 6 Hz, CH_2O); 2.99 (t, 2H, ^3J = 6 Hz, $ArCH_2$). MS (*m/z* (relative intensity)): 148 (86, $M^{+\bullet}$), 118 (100, $M^{+\bullet} - H_2CO$), 90 (59, $M^{+\bullet} - H_2CO - CO$). IR (neat; ν, cm^{-1}): 1720 (C=O).

X-ray Data Collection, Structure Determination, and Refinement of $[PdBr\{C_6H_4(CH_2CH_2OH)\text{-}2\}(tmeda)]$ (1). X-ray data were collected for a yellowish crystal fragment (cut from a large block) glued on top of a glass fiber on an Enraf-Nonius CAD4 diffractometer at 295 K. Unit cell parameters were determined from a least-squares treatment of SET4 setting angles of 25 reflections in the range 12.5° < θ < 19.5° and checked for higher lattice symmetry.[47] Data were corrected for Lp and absorption (DIFABS[48] correction range 0.86–1.15). The structure was solved with the PATT option of SHELXS86[49] and refined by full-matrix least squares on *F* with SHELX76.[50] Hydrogen atoms were taken into account at calculated positions, except for the hydroxylic H, which was located from a difference map, and its positional and isotropic thermal parameters were refined. Convergence was reached at *R* = 0.024. The alternative absolute structure was rejected based on higher final *R* values. Crystal and numerical data on the structure determination have been collected in Table II. Neutral atom scattering factors were taken

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Table II. Crystal Data and Details of the Structure Determination

	1	3
	Crystal Data	
empirical formula	$C_{14}H_{25}BrN_2OPd$	$C_{14}H_{25}N_2OPd{\cdot}NO_3$
fw	423.69	405.79
cryst syst	monoclinic	orthorhombic
space group	*Cc* (No. 9)	$P2_1ab$ (nonstd setting of $Pca2_1$ (No. 29))
a, Å	12.412(1)	9.679(1)
b, Å	10.391(1)	11.903(2)
c, Å	13.441(1)	14.501(2)
β, deg	106.43(1)	
V, Å^3	1662.7(3)	1670.6(4)
Z	4	4
D_{calc}, g cm^{-3}	1.692	1.613
$F(000)$, e	848	832
μ(Mo Kα), cm^{-1}	34.8	11.2
cryst size, mm	0.30 × 0.40 × 0.50	0.15 × 0.23 × 0.75
	Data Collection	
temp, K	295	100
radiation (Mo Ka; Zr filtered), Å	0.710 73	0.710 73
θ_{min}, θ_{max}, deg	0.1, 28.4	1.41, 27.50
scan type	$\omega/2\theta$	$\omega/2\theta$
$\Delta\omega$, deg	$0.60 + 0.35 \tan\theta$	$0.60 + 0.35 \tan\theta$
horiz and vert aperture, mm	3.00, 6.00	3.00, 5.00
ref rfln(s)	–3,4,–5; 245	320; 4,0,–2; 0,–2,3
data set	*h*, –16 to 0; *k*, 0–13; *l*, –17 to 17	*h*, 0–12; *k*, 0–15; *l*, 0–18
total no. of data; unique no. of data	2140; 1933	2211; 2035
no. of obsd data ($I > 2.5\sigma(I)$)	1875	1635
	Refinement	
no. of refined params	188	215
R, R_w, S	0.024, 0.026, 1.45	0.0245, 0.0238, 1.17
weighting scheme, w^{-1}	$\sigma^2(F)$	$\sigma^2(F)$
$(\Delta/\sigma)_{av}$	0.03	0.035
min and max residual density, e Å^{-3}	–0.70, 0.36	–0.54, 0.82

Table III. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for the Non-H Atoms of 1

atom	x	y	z	U_{eq},[a] Å^2
Pd	0	–0.05794(3)	$^1/_2$	0.0270(1)
Br	0.01689(6)	0.15862(6)	0.43753(5)	0.0455(2)
O	0.1524(5)	0.2958(5)	0.6650(4)	0.0616(19)
N(1)	–0.1734(5)	–0.0821(5)	0.4037(5)	0.0386(17)
N(2)	–0.0252(4)	–0.2402(4)	0.5603(4)	0.0369(14)
C(1)	0.1602(6)	–0.0524(5)	0.5840(5)	0.0333(17)
C(2)	0.1973(5)	0.0072(5)	0.6818(4)	0.0324(17)
C(3)	0.3108(5)	–0.0037(6)	0.7379(5)	0.0437(17)
C(4)	0.3863(5)	–0.0713(6)	0.6976(6)	0.0506(19)
C(5)	0.3501(5)	–0.1276(6)	0.6015(5)	0.0478(19)
C(6)	0.2382(5)	–0.1154(6)	0.5467(5)	0.0425(19)
C(7)	0.1191(5)	0.0807(5)	0.7290(5)	0.0430(19)
C(8)	0.1545(6)	0.2212(6)	0.7533(5)	0.052(2)
C(9)	–0.1981(6)	–0.2202(6)	0.4140(5)	0.0503(19)
C(10)	–0.1488(5)	–0.2633(6)	0.5261(5)	0.0474(19)
C(11)	–0.2509(6)	0.0001(8)	0.4437(7)	0.064(3)
C(12)	–0.1898(7)	–0.0514(8)	0.2931(5)	0.062(3)
C(13)	0.0342(6)	–0.3452(6)	0.5206(6)	0.054(2)
C(14)	0.0126(7)	–0.2439(7)	0.6749(5)	0.058(2)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i{\cdot}\mathbf{a}_j$.

from Cromer and Mann[51] and corrected for anomalous dispersion.[52] Final coordinates and equivalent isotropic thermal parameters for 1 are given in Table III.

Table IV. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for the Non-H Atoms of 3

atom	x	y	z	U_{eq},[a] Å^2
Pd	0.5	0.91237(2)	0.24934(3)	0.0143(1)
O(1)	0.4536(4)	0.7422(3)	0.2448(3)	0.0251(10)
N(1)	0.5123(12)	0.9090(3)	0.4002(3)	0.0210(16)
N(2)	0.5116(13)	1.0852(3)	0.2641(3)	0.0225(16)
C(1)	0.4951(14)	0.9122(4)	0.1131(3)	0.0160(14)
C(2)	0.3906(7)	0.8517(5)	0.0701(4)	0.0207(17)
C(3)	0.3870(6)	0.8424(4)	–0.0265(3)	0.0223(16)
C(4)	0.4877(9)	0.8925(4)	–0.0800(3)	0.0283(16)
C(5)	0.5956(7)	0.9502(4)	–0.0388(4)	0.0280(17)
C(6)	0.6005(6)	0.9598(4)	0.0565(3)	0.0217(17)
C(7)	0.2867(6)	0.7898(4)	0.1285(3)	0.0217(16)
C(8)	0.3535(6)	0.6955(4)	0.1813(3)	0.0213(16)
C(9)	0.5311(8)	1.0284(4)	0.4261(3)	0.035(2)
C(10)	0.4578(7)	1.1030(5)	0.3633(3)	0.041(2)
C(11)	0.3887(6)	0.8612(6)	0.4424(4)	0.0273(19)
C(12)	0.6338(8)	0.8434(6)	0.4291(5)	0.031(2)
C(13)	0.3970(8)	1.1400(7)	0.2148(7)	0.055(3)
C(14)	0.6365(7)	1.1401(7)	0.2369(6)	0.051(3)
O(2)	0.0810(5)	0.1034(3)	0.3383(3)	0.0370(14)
O(3)	0.1070(4)	–0.0714(3)	0.3060(3)	0.0310(14)
O(4)	–0.0938(5)	–0.0055(4)	0.3358(3)	0.0490(16)
N(3)	0.0297(5)	0.0096(4)	0.3265(3)	0.0217(14)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i{\cdot}\mathbf{a}_j$.

X-ray Data Collection, Structure Determination, and Refinement of [Pd{$C_6H_4(CH_2CH_2OH)$-2}(tmeda)]NO_3 (3). A yellow rod-shaped crystal was mounted on top of a glass fiber and transferred to an Enraf-Nonius CAD4 diffractometer for data collection at 100 K. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections in the range 13.9° < θ < 17.9° and checked for higher lattice symmetry.[47] Data were corrected for Lp and for a small linear increase (1.7%) of the intensity control reflections during the 31 h of X-ray exposure time but not for absorption. The structure was solved with standard Patterson methods (SHELXS86)[49] and a series of subsequent difference Fourier analyses. Refinement on F was carried out by full-matrix least-squares techniques. Carbon-bonded H atoms were introduced on calculated positions (C–H = 0.98 Å) and included in the refinement riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters and (C-bonded H atoms with one common isotropic thermal parameter (U = 0.035(3) Å^2). The hydroxylic H atom was located from a difference map and included in the refinement with free positional parameters and an individual isotropic thermal parameter. Weights were introduced in the final refinement cycles; convergence was reached at $R = 0.0245$, $R_w = 0.0238$. The absolute structure was checked by refinement with opposite anomalous dispersion factors ($-if''$) resulting in $R = 0.0248$, $R_w = 0.0241$. Crystal data and numerical details of the structure determination are given in Table II. Neutral atom scattering factors were taken from Cromer and Mann[51] and corrected for anomalous dispersion.[52] All calculations were performed with SHELX76[50] and PLATON[53] (geometrical calculations and illustrations) on a MicroVax-II cluster. Final coordinates and equivalent isotropic thermal parameters for 3 are given in Table IV.

Acknowledgment. We thank the Innovation Oriented Research Program on Catalysis for financial support (to P.L.A.) The Netherlands Foundation for Chemical Research (SON) and the Netherlands Organization for Scientific Research (NWO) are thanked for financial support (to W.J.J.S. and A.L.S.). X-ray data were kindly collected by A. J. M. Duisenberg.

Supplementary Material Available: Tables of fractional coordinates for the hydrogen atoms, anisotropic thermal parameters, and bond distances and angles of 1 and 3 (8 pages). Ordering information is given on any current masthead page.

OM920603M

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