Hydrogen Bonding and Conformational Analysis of Chelate-Stabilized Alkoxopalladium(II) Complexes Derived from Amino Alcohol Ligands

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The reaction of palladium acetate with two equivalents of di- and triethanolamines $RN(CH_2CH_2OH)_2$ in the presence of a base affords the new chelate-stabilized alkoxo Pd(II) complexes $[Pd(OCH_2CH_2N(R)CH_2CH_2OH)_2]$ [R = Me (**1**), Et (**2**), *n*-Bu (**3**), benzyl (**4**) or CH_2CH_2OH (**5**)]. These *N,O*-ligated complexes are isolated in high yield as yellow, crystalline solids and are thermally stable despite the presence of several β-hydrogen atoms in the ligand system. Both complexes possess a square-planar palladium coordination geometry with the two oxygen atoms positioned mutually *trans*. The most notable difference in the molecular structures is that **1** forms a two dimensional network of intermolecular O−H···O hydrogen bonds, whereas **5** forms intramolecular O−H···O hydrogen bonds, which cage the palladium center. In solution **1**−**4** exist as a diastereoisomeric mixture (a racemic enantiomeric pair S_NS_N, R_NR_N and a mesomeric form R_NS_N) in a 1:1 molar ratio, and this ratio is independent of temperature in nonalcoholic solvents. When complexes **1**−**4** are dissolved in protic solvents (e.g. MeOH) the diastereomeric excess is temperature-dependent due to an exchange process between the *meso* diastereoisomer and the (racemic) enantiomeric pair. Thermodynamic parameters for this process in a mixture of MeOH-toluene have been determined with NMR and show this process to be influenced by the steric nature of the alkyl substituent (R) on nitrogen. A conformational analysis based on ^{1}H-NMR coupling constants within the *N,O*-chelate ring of complexes **1**−**4** provides details on the solution structure of the ring in both diastereoisomers.

Introduction

The nature of O−H···O hydrogen bonding has attracted attention in inorganic and organometallic chemistry and it has been shown that such bonding exercises important effects on the properties and organization of several metal complexes[1]. However, the use of hydrogen bonds as a steering force in the assembly of individual molecules into two or three dimensional structures is still difficult, although important progress has been made in the last few years[2]. Nevertheless there is still need for a better understanding of O−H···O bonding, and ideal materials for investigating the nature of hydrogen bond interactions are transition metal alkoxides, since the polar character of the M−O bond provides a strong tendency for O−H···O hydrogen bond formation (see Figure 1)[3]. Another reason for the recent interest in the nature and properties of late transition metal alkoxide complexes is that a number of metal-catalyzed organic reactions involve these species as intermediates[4].

In the course of our study on palladium(II) alkoxide and aryloxide complexes containing bidentate *N*-donor ligands[5], and in particular our study on the role of O−H···O hydrogen bonding and its stabilizing effect on the Pd−O bond, we set out to synthesize and study the reactivity of

Figure 1. Association equilibrium for metal alkoxides with alcohols

alkoxopalladium(II) complexes derived from amino alcohol ligands. Amino alcohol chelate metal complexes form an important class of complexes[6], some of which have been shown to have interesting catalytic activity[7]; the most recent applications include the synthesis of chiral epoxides[7a] and enantioselective addition of dialkylzinc to aldehydes[7b]. Furthermore, it is known that amino alcohols, such as 2,2′-methyliminodiethanol and 2,2,2-nitrilotriethanol, readily form complexes with transition metals and that these complexes often show the presence of O−H···O hydrogen bonds that stabilize the structure as a whole[8]. Recently, Pringle et al. reported the isolation of chelate-stabilized alkoxopalladium(II) complexes derived from phosphinoalcohols, in which hydrogen bond interactions were present[9].

The present study shows that amino alcohols of the type $RN(CH_2CH_2OH)_2$ can be deprotonated to form anionic chelating ligands for palladium alkoxide units and that in the new complexes, in addition to the expected *N,O*-chelate coordination, the free CH_2CH_2OH arm becomes involved in interesting inter- and intramolecular O−H···O hydrogen bonding.

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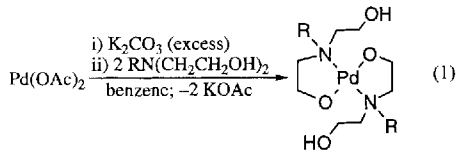
Preparation of the Alkoxopalladium(II) Complexes

The 2:1 molar reaction of 2,2′-methyliminodiethanol, 2,2′-ethyliminodiethanol, 2,2′-*n*-butyliminodiethanol, 2,2′-benzyliminodiethanol or 2,2,2-nitrilotriethanol with palladium acetate in the presence of K_2CO_3 as a base affords new *N,O*-chelated complexes $[Pd(OCH_2CH_2N(R)CH_2CH_2OH)_2]$ [R = Me (**1**), Et (**2**), n-Bu (**3**), CH_2Ph (**4**) and CH_2CH_2OH (**5**)], which have been isolated as yellow, crystalline complexes in high yields (see eq. 1).



(1)

1: R = Me
2: R = Et
3: R = Bu
4: R = Benzyl
5: R = CH_2CH_2OH

These thermally stable complexes (m.p. >113 °C) have been characterized by elemental analysis, ^1H and ^{13}C-NMR and IR spectroscopy and for **1** and **5** by X-ray crystal structure analysis. From these data it has been unambiguously established, both in solution and the solid state, that in the new complexes two anionic O atoms are bound to palladium in mutually *trans* positions (vide infra) with the coordination sphere of the metal center being completed by coordination of the nitrogen atom from both ethanolamine ligands (i.e. formation of a 5-membered $PdOCH_2CH_2N$ chelate ring). The coordinated nitrogen atoms are stereogenic centers and complexes **1**–**4** exist as diastereoisomers. The terminal CH_2CH_2OH groups have no interaction with the metal center but they do produce various types of O–H···O hydrogen bonds, which provide stabilization of these complexes (vide infra).

Molecular Structures of 1 and 5

In order to establish the nature of O–H···O hydrogen bonding in the *N,O*-ligated palladium(II) complexes in the solid state, single crystal X-ray diffraction studies of $[Pd(OCH_2CH_2N(Me)CH_2CH_2OH)_2]$ (**1**) and $[Pd(OCH_2CH_2N(CH_2CH_2OH)_2)_2]$ (**5**) were carried out. The molecular structures of these complexes together with the adopted numbering schemes are shown in Figures 2 and 3, respectively. Important bond lengths and bond angles are collected in Table 1. It is worth reemphasizing that the *N*-donor atoms in **1**–**4** are stereogenic centers and crystallization of complex **1** affords the R_NR_N and S_NS_N racemate (enantiomeric pairs) of which the S_NS_N enantiomer is shown in Figure 2.

Complexes **1** and **5** both contain two *N,O*-chelate bonded amino alcoholate ligands and the palladium center possesses an approximately square-planar coordination geometry with adjacent, interligand angles around the metal center falling in the range 85.4–94.6°. In these compounds the arrangement of the 5-membered $PdOCH_2CH_2N$ chelate rings is such that the two anionic O atoms, and consequently the two N donor atoms, are positioned *trans* to each other. This *trans* arrangement is often encountered in palladium bis(amine) complexes such as *trans*-$[Pd(OAc)_2(Et_2NH)_2]$[13] and *trans*-$[Pd(OPh)_2(pyrrolidine)_2]$[5d] which contain two anionic oxygen donor atoms and monodentate amine donor ligands; the *cis* arrangement has been found in palladium complexes where N~N chelating amine ligands have been used[5a,b].

Figure 2. An ORTEP drawing (50% probability level) of the molecular structure of $[Pd(OCH_2CH_2N(Me)CH_2CH_2OH)_2]$ (**1**) together with the adopted numbering scheme

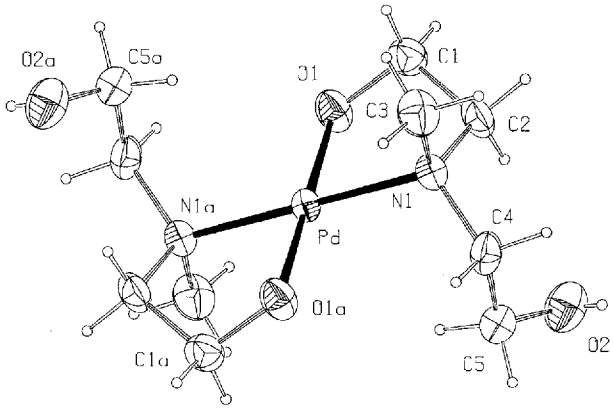
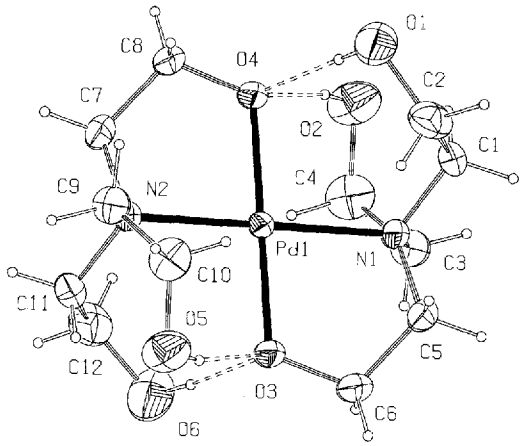


Figure 3. An ORTEP drawing (50% probability level) of the molecular structure of $[Pd(OCH_2CH_2N(CH_2CH_2OH)_2)_2]$ (**5**) together with the adopted numbering scheme



The main structural difference between complexes **1** and **5** is found in the positioning of the O–H···O hydrogen bonds that results from the presence of the uncoordinated CH_2CH_2OH groups. In complex **5** the four terminal hydroxyl units are intramolecularly hydrogen bonded to the palladium-bound anionic oxygen atom in such a way that the alkyl chains form a cage around the metal center. However, in complex **1** the hydroxyl units form infinite planes of intermolecular O–H···O hydrogen bonds throughout the crystal lattice by bonding to a palladium-bound anionic oxygen atom of a neighbouring molecule (see Figure 4).

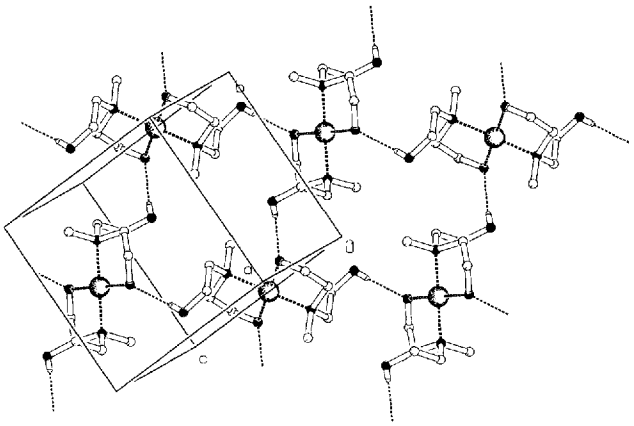
The neighbouring planes of O–H···O hydrogen bonds in **1** are oriented in an antiparallel fashion, thereby producing a puckered layer. The appearance of this two-dimensional

Table 1. Selected bond distances (Å), bond angles (deg) and dihedral angles (deg) for the *N,O*-ligated palladium complexes $[Pd(OCH_2CH_2N(Me)CH_2CH_2OH)_2]$ (**1**) and $[Pd(OCH_2CH_2N(CH_2CH_2OH)_2)_2]$ (**5**)[a]

	1	5
Bond Distances		
Pd–O	2.002(3)	2.002(2), 2.003(2)
Pd–N	2.063(3)	2.081(2), 2.081(2)
C–O[b]	1.403(5)	1.420(3), 1.422(3)
C–O[c]	1.409(6)	1.405(4), 1.414(4) 1.413(4), 1.403(5)
O···O	2.652(5)	2.657(3), 2.735(3) 2.687(4), 2.684(4)
Bond Angles		
Pd–O–C	109.4(2)	111.0(1), 110.3(2)
O–Pd–N[b]	85.4(1)	85.6(1), 85.8(1)
O–Pd–N	94.6(1)	94.2(1), 94.5(1)
O–Pd–O	180.00[d]	179.6(1)
N–Pd–N	180.00[d]	179.7(2)
O–H···O	177(7)	179(4), 167(4) 172(4), 164(4)
Dihedral Bond Angles		
N–C–C–O[b]	−53.1(4)	−51.2(3), 52.5(3)
N–C–C–O[c]	80.8(5)	−96.4(3), 59.7(4) −57.8(4), 91.0(4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. – [b] Within the *N,O* chelate ring. – [c] Within the CH_2CH_2OH unit. – [d] Result of symmetry operation: 1 − x, 1 − y, −z.

Figure 4. Diagram of the crystal packing for **1** showing the two-dimensional network of intermolecular O–H···O hydrogen bonds



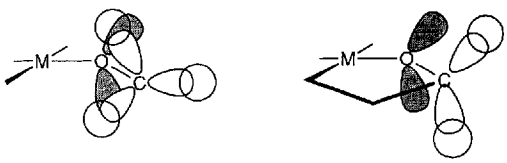
aggregate in complex **1** is a consequence of directional, O–H···O interactions [O(2)···O′(1) = 2.652(5) Å; O(2)–H(24)···O′(1) = 177(7)°]. Similar directional interactions have recently been reported for the assembly of individual molecules of malate anions through use of O–H···O hydrogen bonds that leads to the formation of two and three-dimensional structures[14]. We anticipated that the presence of two more CH_2CH_2OH arms in complex **5** would lead to a three-dimensional aggregate held together by hydrogen bonds, but have found instead that this generates a cage of intramolecular O–H···O hydrogen bonds around the palladium center.

The results show that it is difficult to control the steering forces of O–H···O hydrogen bonds for the assembly of larger aggregates and that the importance of the various factors controlling these processes are still not well understood. Complex **1** reveals the presence of an intramolecular C–H···O interaction from a NCH_2 group of the chelate ring with the oxygen of the "free" NCH_2CH_2OH group [C(2)–H(2)···O(2) 3.119(5) Å]. Similar intramolecular C–H···O interactions are found in **5**, but there is one important difference compared to **1**. In **5** the NCH_2 group of the NCH_2CH_2OH arm forms its interaction not with the oxygen atom of the chelate ring (as in **1**) but with the oxygen of a neighbouring CH_2CH_2OH arm of the same ligand [C(1)–H(11)···O(2) 3.188(4) Å and C(11)–H(12)···O(5) 3.159(4) Å]. In related studies we have recently reported other examples of C–H···O interactions in $[Pd\{OCH(CF_3)_2\}(OC_6H_5)(bpy)]\cdot HOC_6H_5$[5a] and $[Pd(Me)\{OCH(CF_3)_2\}(tmeda)]$[5c] and one might conclude that this type of additional electrostatic interaction is important in stabilizing late transition metal alkoxides. It is worth noting that the nature and importance of not only C–H···O interactions but also C–H···M and related hydrogen bond interactions is the subject of much current discussion[15].

The O···O distances in complexes **1** and **5** [2.652(5) Å and 2.657(3)–2.735(3) Å, respectively] are comparable to O···O distances in organic molecules[16] and late transition metal alkoxide alcohol adducts[3-4] displaying hydrogen bonding. Hydrogen bonds are referred to as strong when the O···O distance is in the range 2.50–2.65 Å[16e], and on this basis we conclude that the O–H···O interactions in **1** and **5** are reasonably strong.

The C–O bond lengths (1.403–1.422 Å) in **1** and **5** are significantly longer than C–O bond lengths reported for platinum and iridium alkoxide complexes (1.33–1.37 Å)[17], but are almost identical to C–O bond lengths in lithium and sodium alkoxides (ca. 1.41 Å)[18]. Wiberg showed that in late transition metal alkoxide complexes, an interaction between the lone pairs of an oxygen atom of the alkoxide ligand and the rear of a C–H bond of an adjacent alkyl ($-CH_3$ or $-CH_2R$) group results in an attractive Coulombic interaction, that shortens the C–O bond[19] (see Figure 5; discussion of this effect in palladium alkoxides, see ref.[5d]).

Figure 5. Schematic representation of the staggered conformation in a methoxide complex (left) and the eclipsed conformation of an alkoxide that is part of a five-membered chelate ring (right)



The methyl group of a methoxide ligand is free to adopt a staggered conformation (with respect to the O lone pairs) which allows this type of interaction and an extreme case of this interaction is found in [Pt(Me)(OMe)(dppe)] where the O–CH_3 bond [1.258(19) Å] approaches double bond character[20]. However, in complexes **1** and **5** where the oxygen atom of the alkoxide ligand is part of a 5-membered chelate ring, this type of interaction will be less efficient since the positioning of the C–H bonds is restricted and they will be partly turned towards an eclipsed position with

respect to the oxygen lone pairs. The C–O bond lengths in **1** and **5** are comparable to that in $[Pt(OCH_2CH_2PPh_2)_2]$ [C–O = 1.413(10) Å][21], where the oxygen atom is also part of a five-membered ring. These bond lengths in **1** and **5** fit in with the empirical observation by Wiberg that in metal alkoxides the conformation of the (O)R group (staggered or eclipsed) seems to determine the observed C–O bond length; i.e. a staggered conformation leads to a C–O distance of less than 1.35 Å and an eclipsed conformation (O atom is part of a chelate ring) affords a C–O distance of more than 1.35 Å[19].

Solution Studies

^1H and ^{13}C-NMR data of the *N,O*-ligated complexes $[Pd(OCH_2CH_2N(R)CH_2CH_2OH)_2]$ [R = Me (**1**), Et (**2**), n-Bu (**3**), CH_2Ph (**4**) and CH_2CH_2OH (**5**)] are found in Tables 2 and 3, respectively. The number and multiplicity of the signals are consistent with the illustrated geometry (see Figure 3) in which there are two anionic *N,O*-bonded $OCH_2CH_2N(R)CH_2CH_2OH$ ligands with "free" CH_2CH_2OH substituents. The absence of coordination of the latter to palladium is evident from the coupling constants (*ddd* patterns with J_{gem} = 11 Hz and J_{vic} = 7 and 2 Hz) of the four CH_2 multiplets at ca. δ = 4.7, 3.9, 2.7 and 1.6. Furthermore, in these complexes the five-membered Pd–OCH_2CH_2N chelate ring produces a series of ^1H-NMR coupling patterns (multiplets) for four inequivalent protons with two multiplets at comparatively low field at δ = 3.6–3.4 and 3.3–3.0 and two at high field at δ = 2.4–2.1 and 1.6–1.4 (conformational analysis, based on the coupling constants of these protons is presented below). Based on substituent additivity parameters and comparison of data with other complexes one can deduce that the NCH_2 proton resonances are those at lower field and those of the CH_2O protons are at higher field; the identification of the pairs of geminal proton resonances was afforded by ^1H-^1H COSY experiments.

The reason that all individual CH_2 protons in these complexes are anisochromous is that the central N atom of the amino alcoholate is coordinated to palladium; it thereby becomes a stable tetrahedral array, i.e. a stereogenic center. In each complex there are thus two stereogenic centers present and each of the complexes **1**–**4** exists as a diastereomeric mixture (see Figure 6). In the ^1H ($CDCl_3$) and ^{13}C-NMR ([D_6]benzene) spectra one observes two separate patterns in a 1:1 intensity ratio for the enantiomeric pair (S_NS_N and R_NR_N) and the mesomeric form (S_NR_N). We have not assigned the two patterns to the individual diastereomers and have designated the more upfield pattern as isomer **1a**–**4a** and the more downfield pattern as isomer **1b**–**4b**. Complex **5** exists as a single diastereoisomer since there are two equivalent CH_2CH_2OH substituents on each nitrogen atom which is therefore not a stereogenic center.

The ^1H-NMR spectra of complexes **1**–**5** shows the presence of O–H···O hydrogen bonds and the O–H resonances appear as broad signals at ca. δ = 8.0, which is ca. 3.5 ppm downfield from their position in the ^1H-NMR spectra of the free amino alcohols. Similar low field shifts of an O–H hydrogen have been reported for related late transition metal alkoxide or aryloxide complexes in which an alcohol is associated through O–H···O hydrogen bonding with the oxygen atom of the alkoxide or aryloxide unit[3–5]. However, the resonance position of the O–H hydrogen in **1**–**5** is less shifted to low field than the corresponding resonance in other late transition metal alkoxide adducts. We believe that this is an indication for the presence of weak O–H···O hydrogen bonds in solution for **1**–**5**. When measured in dry $CDCl_3$ or [D_8]toluene the O–H resonance of **1**–**5** is seen as a triplet due to coupling with the protons of the adjacent CH_2O unit. However, when a trace of water is present the coupling information is lost as the O–H signal becomes broadened due to exchange processes. Similarly, when [D_4]MeOH is added to a solution of complexes **1**–**4** in $CDCl_3$ or [D_8]toluene, the O–H hydrogen is rapidly ex-

Table 2. ^1H-NMR data for the diastereoisomers of the complexes **1**–**4**[a]

Nr.	chelate ring[b]				-NCH_2CH_2OH					R substituent		
	PdOCH_2		CH_2NPd		OCH_2[c]		CH_2N[c]		OH[d]			
	H_d	H_c	H_a	H_b								
1a	3.47	3.04	2.24	1.62	4.57	3.80	2.72	1.43	7.92	2.30 (s, CH_3)		
1b	3.39	3.15	2.05	1.76	4.21	3.80	2.78	1.48	7.98	2.32 (s, CH_3)		
2a	3.51	3.10	2.46	1.28	4.69	3.82	2.76	1.67	7.95	1.97, 1.92 (q, CH_2)[e]	1.25 (t, CH_3)[e]	
2b	3.43	3.10	2.41	1.41	4.42	3.85	2.70	1.74	7.85	2.12, 2.06 (q, CH_2)[e]	1.22 (q, CH_3)[e]	
3a	3.53	3.14	2.57	1.45	4.88	4.00	2.79	1.78	8.05	2.30-2.00 (m, CH_2)	1.70-1.50 (m, CH_2)	0.90 (t, CH_3)[e]
3b	3.50	3.03	2.48	1.54	4.48	4.00	2.74	1.82	7.85	2.30-2.00 (m, CH_2)	1.70-1.50 (m, CH_2)	0.90 (t, CH_3)[e]
4a	3.58	2.98	2.79	1.40	4.83	4.00	2.72	1.85	7.95	7.56 (dd, *ortho-H*)[f]	7.1-7.0 (m, aryl-*H*)	4.43, 3.12 (d, CH_2)[g]
4b	3.54	2.98	2.75	1.47	4.55	4.00	2.75	1.95	7.95	7.50 (dd, *ortho-H*)[f]	7.1-7.0 (m, aryl-*H*)	4.52, 4.42 (d, CH_2)[g]

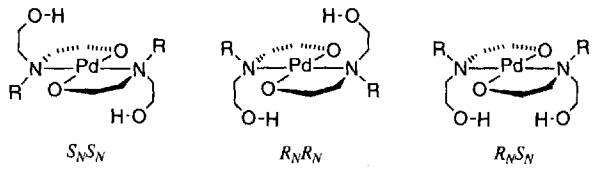
[a] At 300 MHz in [D_6]benzene at room temperature. – [b] The coupling constants (J_{gem}, J_{gauche} and J_{trans}) within the chelate ring are summarized in Table 4 (conformational analysis of complexes **1**–**4**); H_a (axial) and H_b (equatorial) are from the CH_2O fragment and H_c (axial) and H_d (equatorial) are from CH_2N fragment within the chelate ring. – [c] The protons of the noncoordinated CH_2CH_2OH groups appear as *ddd* patterns with characteristic values for the coupling constants (J_{gem} = 11 Hz, J_{vic} = 7 and 2 Hz). – [d] Resonances usually broad (linewidth ca. 15 Hz) though triplet structure is sometimes observed; at higher temperatures they move to lower frequency and for each diastereoisomeric pair also exhibit coalescence behaviour. – [e] J = 7 Hz. – [f] J = 8 and 2 Hz. – [g] J = 13 Hz (AB system).

Table 3. ^{13}C-NMR data for the diastereoisomers of the complexes **1**–**4**[a]

Nr.	$N(CH_2)_2O$	$(CH_2)_2OH$	R substituent	Nr.	$N(CH_2)_2O$	$(CH_2)_2OH$	R substituent
1a	70.8, 65.1	63.3, 60.7	50.6 (CH_3)	**1b**	70.0, 64.9	64.8, 59.6	49.0 (CH_3)
2a	65.1, 65.0	61.1, 60.0	54.7 (CH_2), 10.5 (CH_3)	**2b**	65.1, 64.7	60.8, 59.6	53.6 (CH_2), 10.5 (CH_3)
3a	66.1, 65.2	60.9, 60.1	60.2 (NCH_2), 26.6 (CH_2) 20.5 (CH_2), 14.0 (CH_3)	**3b**	65.6, 65.2,	61.2, 59.2	59.6 (NCH_2), 26.4 (CH_2) 20.5 (CH_2), 14.0 (CH_3)
4a	65.8, 65.1	61.5, 59.6	64.1 (CH_2), 128.5 (*m*-C) 128.7 (*p*-C), 132.6, (*o*-C) 132.0 (*ipso*-C)	**4b**	65.1, 65.1	60.9, 60.4	64.0 (CH_2), 128.4 (*m*-C) 128.6 (*p*-C), 132.7, (*o*-C) 132.2 (*ipso*-C)

[a] All measurements at 300 MHz in $CDCl_3$ at room temperature.

Figure 6. Diastereoisomers of *N,O*-ligated complexes **1**–**4**



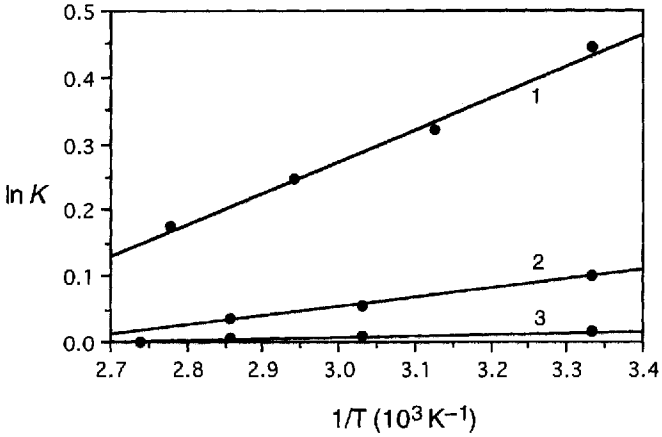
changed for deuterium. Furthermore, the O–H hydrogen signal of complexes **1**–**4** in $CDCl_3$ moves to higher field upon heating, and this is consistent with a shift of the association equilibrium towards a situation without O–H···O hydrogen bonds (see Figure 1).

Interestingly low temperature ^{1}H-NMR spectra of complex **5** in $CDCl_3$ do reveal the presence of two different O–H···O hydrogen bonds (δ_{OH} = 6.82 and 6.90 at 254 K) for the CH_2CH_2OH substituents, which we had anticipated would be equivalent. We believe that this could be due to the formation of both intra- and intermolecular O–H···O hydrogen bonds. These relatively small downfield shifts indicate weaker hydrogen bonds in **5** than in **1**; this is not unexpected since in **5** each alkoxide oxygen atom supports two O–H···O hydrogen bridges rather than one as in **1**. This low temperature NMR phenomenon exhibited by **5** is not demonstrated by complexes **1**–**4**, which have only one CH_2CH_2OH unit. More detailed solution studies of **1**–**5** are needed to evaluate the role of intra- and intermolecular O–H···O hydrogen bonds in these species.

Exchange Between the Diastereoisomeric Forms of Complexes 1–4

^{1}H and ^{13}C-NMR data show that the two individual diastereomers of **1**–**4** (with S_NS_N/R_NR_N and S_NR_N conformations) are present in solution in equal amounts when [D_6]benzene or $CDCl_3$ are used and changing the temperature of these solutions has no influence on this ratio. When a proton donor such as MeOH or H_2O is added to these solutions the diastereomeric excess can, depending upon the R substituent, increase to 65% (R = Bu (**3**), [D_6]benzene) at room temperature. Upon raising the temperature ([D_6]benzene) in the presence of MeOH the diastereomeric excess decreases for all four complexes (R = Bu (**3**); d.e. = 10% at 355 K). These results show that the two diastereoisomers are interconvertible. The operative exchange process could involve either Pd–N dissociation (inversion of N configuration) or Pd–O dissociation (substitution of the free arm for an alkoxide unit). To determine the thermodynamic parameters for this process the ratio of the diastereoisomeric forms of **1** and **3** in [D_8]toluene/[D_4]MeOH (v:v 9:1) has been determined at several temperatures. This ratio is directly related to the equilibrium constant (K) for this process and thermodynamic parameters for the exchange between the two diastereoisomers of **1** and **3** have been derived from the temperature dependence of K through use of a Van't Hoff plot in which $\ln K$ is plotted against $1/T$ (see Figure 7).

Figure 7. Van't Hoff plot for complex with R = Bu (**1**) and R = Me (**2**) in toluene/MeOH with comparative data for R = Bu (**3**) in dry toluene in the absence of MeOH



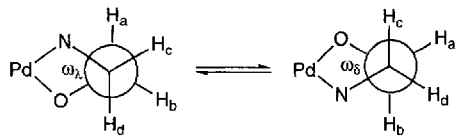
The thermodynamic parameters obtained from Figure 7 for **1** (at 298 K) are $\Delta G^\circ = -1.0$ kJ mol^{-1}, $\Delta H^\circ = -4.0$ kJ mol^{-1} and $\Delta S^\circ = -10.0$ J K^{-1} mol^{-1}, whereas for **3** (at 298 K) they are $\Delta G^\circ = -0.2$ kJ mol^{-1}, $\Delta H^\circ = -1.1$ kJ mol^{-1} and $\Delta S^\circ = -3.0$ J K^{-1} mol^{-1}. From these thermodynamic data is is not possible to conclude whether an intra- or intermolecular process is operative. However, one can clearly see that there is very little difference thermodynamically in the stability of the two diastereoisomers and that in this system formation of O–H···O hydrogen bond-

ing by donor solvents can be used to preferentially stabilize one or the other diastereoisomer.

Conformational Analysis of *N,O*-Chelate Ring Systems

The conformation of five-membered diamine chelate rings in metal complexes ($MNCH_2CH_2N$) has been intensively studied by several techniques[22]. However, only a few reports have appeared concerning five-membered chelate rings that contain oxygen atoms ($MOCH_2CH_2N$). In one report nickel(II) amino alcohol complexes were investigated using ^1H NMR with emphasis on the inversion at oxygen without obtaining quantitative conformational parameters[23]. Hawkins and Palmer in 1978 were the first to analyse conformations of the chelate ring of an metal amino alcohol complex, Co(III)-Ψ-ephedrine, based on the coupling constant method[24]. A five-membered metal chelate ring ($MXCH_2CH_2N$) is characterized by two possible conformations, λ and δ (representing the two enantiomeric forms of a puckered ring), and a dihedral (torsional) angle ω (see Figure 8); in a ^1H-NMR spectrum the CH_2CH_2 group affords two geminal couplings J_{ab}, J_{cd} and four vicinal couplings J_{ac}, J_{bc}, J_{ad} and J_{bd}. From the latter couplings one can determine ω and the mole fraction in the λ (or δ) conformation [n_λ or (n_λ)] through use of the Karplus relation (see Experimental Section).

Figure 8. Newman projections for the λ (left) and δ (right) conformation for a five-membered $MOCH_2CH_2N$ chelate ring



^1H-NMR spectra of the **1**–**4** have been analysed to abstract coupling constant and chemical shift data of the four OCH_2CH_2N protons. This analysis based on spectral simulation also affords a complete assignment of resonances to the individual protons in both diastereoisomers (with S_NS_N/R_NR_N and S_NR_N conformations) of each complex. In order to determine the conformational parameters we used the arithmetic average value of the two vicinal couplings J_{ac} and J_{bd} (3.9 Hz) to help eliminate effects from the unsymmetrical nature of the $PdOCH_2CH_2N$ chelate ring and with use of the Karplus relationship we then calculated n_λ and ω for the chelate ring; these results are summarized in Table 4.

One has to realize that substitution of an oxygen atom for a NR_2 unit in diamine ring systems yields some important differences between the five-membered rings formed by chelation of $OCH_2CH_2NR_2$ and $R_2NCH_2CH_2NR_2$ ligands to metal centers. First, an anionic oxygen atom has, in contrast to the N atom of an NR_2 group, two lone pair orbitals whose preferred orientation will depend on interactions with the rest of the molecule. These lone pair orbitals can influence the structure of the ring by, for example, interacting with the back-side of a C–H bond of the adjacent alkyl, so shortening the C–O bond length[19], or they can take part in O···H–X hydrogen bonding, thus elongating the M–O bond. Second, the M–O bond length in metal alkoxide complexes is in general shorter (0.1–0.2 Å) than the M–N bond length. Therefore the five-membered chelate ring $MOCH_2CH_2N$ adopts an asymmetric structure in which the two ring carbon atoms are no longer equidistant from the N–M–O plane. This asymmetric deformation affects the conformational parameters and generally results in a decrease of the dihedral angle (ω) of the chelate ring[22]. Third, in a $MOCH_2CH_2N$ system the presence of two different donor atoms in the five-membered ring ensures that the vicinal couplings J_{ac} and J_{bd} are not equal, whereas in symmetrical $MNCH_2CH_2N$ chelate ring systems J_{ac} will always be equal to J_{bd}. Other studies have shown that these vicinal couplings have values that are almost independent of temperature or substituent[22]. Since J_{ac} and J_{bd} are essentially constant and independent of the R substituent for complexes **1**–**4**, we have used their average in our conformational analysis.

The first feature one sees from the conformational analysis is that the $PdOCH_2CH_2N$ rings in both diastereoisomers (form a and b) of all complexes **1**–**4** have the λ conformation (n_λ = 0.74–0.99) as the most predominant form. The conformational preference of the NCCO chelate ring for the λ form is influenced by the R substituent with the larger R substituents increasing the mole fraction in the λ conformation. These results indicate that larger R substituents induce more sterical hindrance in the δ conformation than in the λ conformation. Knowing the predominant conformation of the rings in **1**–**4** we can now interpret the original ^1H-NMR chemical shift data of **1**–**4** in more detail and assign equatoiral and axial ring protons unambiguously. What is found is that the NCH_2 axial proton has the lowest field position (H_d in the λ conformation) at δ = 3.6–3.4 and the NCH_2 equatorial proton (H_c) is less shielded and appears at δ = 3.3–3.0. Further, the axial CH_2O proton (H_a) at δ = 2.4–2.1 resonates at lower field than the equatorial CH_2O proton (H_b) at δ = 1.6–1.4. These results contrast with data from diamine chelate ring systems, where the two axial protons resonate at higher field than the two equatorial protons[22]. These relative positionings of the axial and equatorial protons in the ^1H-NMR spectra of **1**–**4** is fully consistent with expected shielding/deshielding by the R substituent in the λ conformation. The overal preference for the λ conformation is the same as that reported by Hawkins et al. for amino alcoholate chelate rings[24] and this preference may be a general feature of *N,O*-chelate systems.

Another aspect of the conformational analysis is that the trend in the chemical shift difference between the axial and equatorial protons [$\Delta\delta_{(eq-ax)} = (\delta_a - \delta_c) < (\delta_d - \delta_b)$] is different than that in diamine chelate ring systems, where $\Delta\delta_{(a-c)}$ is almost equal to $\Delta\delta_{(d-b)}$. In our system the chemical shift difference $\Delta\delta_{(eq-ax)}$ shows a cosine-like relationship to the value of the coupling constant J_{ac} and J_{bd} between an equatorial and an axial proton (see Figure 9) with an increase in $\Delta\delta_{(eq-ax)}$ correlating with a decrease of J_{ac} and J_{bd}.

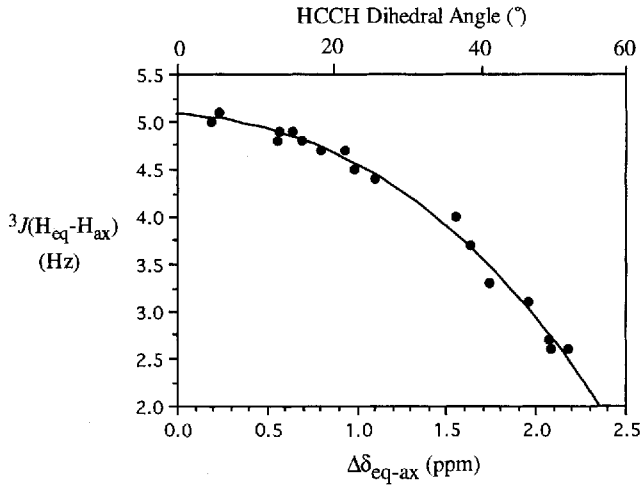
Another conformational parameter obtained from the analysis is ω, which reflects the degree of nonplanarity of

Table 4. Coupling constants within the $PdOCH_2CH_2N$ chelate ring and conformational parameters for diastereoisomers of complexes **1**–**4**[a]

	coupling constants						conformational parameters			
Nr.	J_{ab} (Hz)	J_{cd} (Hz)	J_{ad} (Hz)	J_{ac} (Hz)	J_{bc} (Hz)	J_{bd} (Hz)	ω (°)	η_λ	ΔG_1° (kJ/mol)	ΔG_2° (kJ/mol)
1a	−11.6	−11.5	10.6	4.7	2.6	2.9	51.9	0.89	3.5	10.4
2a	−11.6	−11.3	11.2	4.9	1.8	2.8	51.7	0.96	6.2	15.8
3a	−11.5	−11.4	11.2	4.9	1.7	2.6	51.6	0.97	7.0	17.3
4a	−11.5	−11.4	11.3	5.0	1.4	2.6	51.3	0.99	---	---
1b	−11.6	−11.5	8.9	4.4	4.0	3.7	50.9	0.74	0.9	5.2
2b	−11.6	−11.4	10.2	4.8	3.0	3.1	51.3	0.84	2.4	8.3
3b	−11.6	−11.5	10.2	4.8	2.9	3.1	51.3	0.85	2.6	8.6
4b	−11.5	−11.6	11.0	5.1	2.3	2.7	51.4	0.91	4.1	11.5

[a] Coupling constants measured at 300 MHz in [D_6]benzene at room temperature with a random error estimated as 0.1 Hz. The errors are for w ±0.3°, η_2 ±0.04 and ΔG^0 ±1.0 kJ/mol.

Figure 9. Plot of J_{ac} and J_{bd} vs. chemical shift difference $\Delta\delta_{(ax-eq)}$ of axial and equatorial protons of a CH_2 group



the $PdOCH_2CH_2N$ chelate ring. For all complexes the determined value of ω in both diastereoisomers is 50–52°, and this angle is smaller than that found in related palladium diamine coordination compounds (53–56°). This result is consistent with the unsymmetrical structure of the $PdOCH_2CH_2N$ chelate ring (vide supra). There is no significant change in ω with different R substituents on nitrogen. It is interesting to see that the dihedral angle of 51.9° determined with NMR for **1** (R = Me with n_λ = 0.89) is only slightly smaller than the dihedral angle found in the X-ray structure of this complex (53.1°), which also has a λ conformation.

The conformational parameters of the $PdOCH_2CH_2N$ chelate ring are not very sensitive to temperature or solvent changes. For example for **1a** in [D_6]benzene at 295 K η_λ = 0.89 whereas at 330 K this has descreased only slightly to η_λ = 0.82 and in CD_2Cl_2 or [D_6]acetone at room temperature η_λ is 0.90 and 0.88, respectively.

A final aspect of the conformational analysis is that one can calculate the free energy difference for the λ − δ equilibrium through use of equation 1. To calculate the relative free energies for the three possible configurations (λλ, λδ and δδ) of the complexes **1**–**4** one needs to assume, first, that the free energy necessary for λ − δ inversion of one ring is independent of the conformation of the second ring, except for the statistical entropy term (this latter term in the present case is RT ln2 in favour of the λδ conformation due to the change of symmetry number) and, second, that an equal enthalpy differences exist between the successive species (i.e., ΔH_1 = 1/2 ΔH_2)[22d]. The strain energy minimization studies reported for ruthenium(III) tris-diamine complexes support these assumptions[25]. The free energy differences for the conformations present in solution for our bis(chelated) $M(OCH_2CH_2N)_2$ systems are then given by equations 3 and 4, where ΔG° is now given by eq. 2.

$$\Delta G^\circ = -RT \ln[(1-n_\lambda)/n_\lambda)] \quad (2)$$

$$\lambda\lambda \rightleftharpoons \lambda\delta \qquad \Delta G_1^\circ = \Delta G^\circ - RT \ln 2 \quad (3)$$

$$\lambda\lambda \rightleftharpoons \delta\delta \qquad \Delta G_2^\circ = 2\,\Delta G^\circ \quad (4)$$

The obtained values for ΔG° or complexes **1**–**4**, summarized in Table 4, show that difference in free energy for the λ and δ conformations is small; since the interconversion between these conformations is fast on the NMR timescale one can already conclude that the energy barrier between them is low.

Conclusion

We have established that changes in the number of uncoordinated CH_2CH_2OH units in metal complexes of amino alcoholates induce large differences in the solid state structures and both two-dimensional networks of intermolecular O–H···O hydrogen bonds and cages with intramolecular O–H···O hydrogen bonds have been identified. Analysis of the $PdOCH_2CH_2N$ chelate ring reveals that these have a preferred λ conformation.

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Experimental Section

General: Reactions were performed in an atmosphere of nitrogen using standard Schlenk techniques. Benzene, 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 (p.a) and methanol (p.a) and the materials 2,2′-methyliminodiethanol, 2,2-ethyliminodiethanol, 2,2′-butyliminodiethanol, 2,2′-benzyliminodiethanol, 2,2,2-nitrilotriethanol and Celite (filter-aid) were purchased from Janssen Chimica. ^{1}H (300.14 MHz) and ^{13}C-NMR (75.04 MHz) spectra were recorded on a Bruker AC 300 spectrometer at ambient temperature in NMR solvents ($CDCl_3$, [D$_6$]benzene and [D$_6$]acetone) obtained from ISOTEC Inc. Infrared spectra (KBr discs) were recorded on a Perkin Elmer 283. Elemental analyses were carried out by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

Preparation of [Pd(OCH$_2$CH$_2$N(Me)CH$_2$CH$_2$OH)$_2$] (**1**): To a mixture of $Pd(OAc)_2$ (0.44 g, 2.0 mmol) and K_2CO_3 (3.23 g, 23.4 mmol) in benzene (50 ml) was added a solution of 2,2′-methyliminodiethanol (0.47 g, 4.0 mmol) in benzene (5 ml). After one day of stirring, the yellow suspension was filtered off over Celite and the filtrate was evaporated to dryness under reduced pressure. The resulting solid was washed with pentane (3 × 10 ml) and dried in vacuo. The product was crystallized by slow diffusion of Et_2O into a CH_2Cl_2 solution. The resulting yellow block-shaped crystals were suitable for X-ray diffraction. Yield 0.59 g (88%). M.p.: 142–144 °C (dec). IR (KBr): ν(CO) 1085, 1060; ν(OH) 3200–3000 cm^{-1}. Anal. calc. for $C_{10}H_{24}N_2O_4Pd$: C 35.04, H 7.06; N 8.17; found C 34.75, H 7.18, N 7.81.

Preparation of [Pd(OCH$_2$CH$_2$N(R)CH$_2$CH$_2$OH)$_2$] R = Et (**2**); *n-Bu* (**3**); *PhCH$_2$* (**4**): Prepared in 84–91% yield as a white (**4**) or yellow (**2** and **3**) material following the same route as described for **1** but using 2,2′-ethyliminodiethanol for the synthesis of **2**, 2,2′-*n*-butyliminodiethanol for the synthesis of **3** or 2,2′-benzyliminodiethanol for the synthesis of **4**. M.p. for **2**: 123–125 °C (dec). IR (KBr) **2**: ν(CO) 1095, 1070; ν(OH) 3200–3000 cm^{-1}. Anal. calc. for $C_{12}H_{28}N_2O_4Pd$ **2**: C 38.87, H 7.61, N 7.56; found C 38.87, H 7.43, N 7.61. M.p. for **3**: 113–115 °C (dec). IR (KBr) **3**: ν(CO) 1070; ν(OH) 3200–2900 cm^{-1}. Anal. calc. for $C_{16}H_{36}N_2O_4Pd$ **3**: C 45.02, H 8.50, N 6.56; found C 44.77, H 8.42, N 6.54. M.p. for **4**: 148–150 °C (dec). IR (KBr) **4**: ν(CO) 1085, 1055; ν(OH) 3200–2900 cm^{-1}. Anal. calc. for $C_{22}H_{32}N_2O_4Pd$ **4**: C 53.39, H 6.52, N 5.66; found C 52.68, H 6.71, N 5.51.

Preparation of [Pd(OCH$_2$CH$_2$N(CH$_2$CH$_2$OH)$_2$)$_2$] (**5**): To a solution of 2,2′,2″-nitrilotriethanol (0.66 g, 2.28 mmol) in benzene (50 ml) was added $Pd(OAc)_2$ (0.50 g, 2.24 mmol) and K_2CO_3 (3.50 g, 25.3 mmol), respectively. After one day stirring the yellow suspension was filtered off over Celite and the filtrate was evaporated to dryness under reduced pressure. The resulting solid was washed with pentane (3 × 10 ml) and dried in vacuo. The product was crystallized by slow diffusion of pentane into a CH_2Cl_2 solution. The resulting yellow, block-shaped crystals were suitable for X-ray diffraction. Yield 0.61 g (70%). M.p.: 133–135 °C (dec). IR (KBr): ν(CO) 1090, 1065; ν(OH) 3300–3100 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 6.75 (s br, 2H, O*H*), 4.88 (ddd, 4H, ^2J = 13 Hz, ^3J = 11 Hz, ^3J = 3 Hz, NCH_2), 3.97 (ddd, 4H, ^2J = 13 Hz, ^3J = 5 Hz, ^3J = 2 Hz, NCH_2), 3.43 (dd, ^3J = 12 Hz, ^3J = 5 Hz, NCH_2), 2.94–2.69 (m, 8H, CH_2), 2.59 (dd, 4H, ^3J = 12 Hz, ^3J = 5 Hz, OCH_2). ^{13}C NMR ($CDCl_3$): δ 67.03 (1 C, NCH_2), 64.34 (1 C, OCH_2), 63.64 (2 C, NCH_2), 60.78 (2 C, OCH_2). Anal. calc. for $C_{12}H_{28}N_2O_6Pd$: C 35.78, H 7.01, N 6.96; found C 35.58, H 6.95, N 6.82.

Conformational Analysis of the OCH$_2$CH$_2$N Chelate Ring: ^{1}H NMR spectra of complexes **1**–**4** in [D$_6$]benzene were analyzed after resolution enhancement by Gaussian multiplication. The mole fraction in the λ conformation (η_λ) can be determined by solving the following equations: $\eta_\lambda = [X\cos^2\omega - \cos^2(120 - \omega)]/[\alpha\cos^2(120 + \omega) - \cos^2(120 - \omega)]$ and $\eta_\lambda = [Y\cos^2\omega - \alpha\cos^2(120 + \omega)]/[\cos^2(120 - \omega) - \alpha\cos^2(120 + \omega)]$, where $X = J_{ad}/(J_{ac} + J_{bd})/2)$, $Y = J_{bc}/(J_{ac} + J_{bd})/2)$ and α is the ratio of the Karplus coefficients A_1 and A_2. It was assumed in these calculations that α = 1.2, $\omega_\delta = \omega_\lambda = \omega$ and that the geminal angles Θ_λ and Θ_δ were equal to 120°. The value of 1.2 for α has been used previously for chelate ring systems and is obtained from the average of a number of literature values for J_{trans}/J_{gauche} coupling constants in metal diamine complexes[22,23]. This value for α was also used by Hawkins et al. in the conformational analysis of Co(III)-ψ-ephedrine complexes which contain five-membered amino alcohol chelate rings[24].

Structure Determination and Refinement of **1**: A yellowish block-shaped crystal (0.32 × 0.38 × 0.47 mm) was mounted on top of a glass-fiber and transferred to an Enraf-Nonius CAD4 diffractometer for data collection at 298 K (Zr-filtered Mo*K*α radiation, $\Delta\omega = [1.02 + 0.35\tan\Theta)°]$. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections with $9.20 < \Theta < 17.57°$. The unit cell parameters were checked for the presence of higher lattice symmetry[26]. A total of 2249 reflections were collected ($2.06 < \Theta < 31.90°$; *hkl:* −10:10, −12:0, −13:13). Data were corrected for Lp effects, for a linear decay (14.6%) of the three intensity control reflections during the 101 hours of X-ray exposure time but not for absorption. The structure was solved with direct methods (SHELXS86)[27], and subsequent difference Fourier analyses. Refinement on *F* [with 1340 reflections with $I > 2.5\sigma(I)$] was carried out by full matrix least-squares techniques. The hydroxylic [O(24)] H atom was located from a difference Fourier map and refined with free positional parameters. All other 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; all H-atoms with one common isotropic thermal parameter [U = 0.046(4) Å^2]. Weights were introduced in the final refinement cycles, convergence was reached at R = 0.0315. A final difference Fourier analysis shows no features outside the range −0.62:0.48 e/Å^3.

Structure Determination and Refinement of **5**: A yellow block-shaped crystal (0.21 × 0.28 × 0.37 mm) was mounted on top of a glass-fiber and transferred to an Enraf-Nonius CAD4 diffractometer for data collection at 298 K (Zr-filtered Mo*K*α radiation, $\Delta\omega = (0.63 + 0.35\tan\Theta)°$). Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections with $10.42 < \Theta < 15.61°$. The unit cell parameters were checked for the presence of higher lattice symmetry[26]. A total of 6144 reflections were collected ($1.54 < \Theta < 27.50°$; *hkl:* −12:12, −17:0, −17:17) and merged (R_i = 0.035) into a dataset of 3559 unique reflections. Data were corrected for Lp effects, for a linear decay (0.7%) of the three intensity control reflections during the 83 h of X-ray exposure time but not for absorption. The structure was solved with Patterson methods (DIRDIF-PATTY)[28], and subsequent difference Fourier analyses: Refinement on F^2 with all 3559 unique reflections was carried out by full matrix least-squares techniques. The four hydroxylic H atoms were located from difference Fourier maps and refined with free positional and thermal

parameters. All other 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. Weights were introduced in the final refinement cycles, convergence was reached at $R_1 = 0.0250$ (calculated for 2471 $F_o > 4\sigma(F_o)$; $wR_2 = 0.0617$, $S = 0.963$). A final difference Fourier analysis shows no features outside the range −0.72:0.49 e/Å^3.

Table 5. Crystal data and details on structure determination for **1** and **5**

	1	**5**
Empirical Formula	$C_{10}H_{24}N_2O_4Pd$	$C_{12}H_{28}N_2O_6Pd$
Formula Weight	342.73	402.78
Space Group	$P2_1/n$ (No. 14)	$P2_1/c$ (No.14)
Crystal System	monoclinic	monoclinic
Z	2	4
a [Å]	7.7502(4)	9.2906(10)
b [Å]	8.7601(4)	13.2629(10)
c [Å]	9.9081(4)	13.4046(10)
b [deg]	95.003(4)	109.77(1)
V [Å^3]	670.12(6)	1554.3(3)
D_{calcd} [g cm^{-3}]	1.699	1.721
$F(000)$	352	832
m_{calcd} [cm^{-1}]	13.7	12.2
Radiation (Mo Ka) [Å]	0.71073 (Zr-filtered)	0.71073 (Zr-filtered)
T [K]	298	298
R_F[a]	0.0315	0.0250
R_{wF}/R_{wF}	0.0335[b]	0.0617[c]

[a] $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. – [b] $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma(wF_o^2)]^{1/2}$. – [c] $R_{wF^2} = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

Crystal data and numerical details of the structure determinations of **1** and **5** are given in Table 5. Neutral atom scattering factors for **1** were taken from Cromer and Mann[29] and corrected for anomalous dispersion[30]. Scattering factors and anomalous dispersion factors for **5** were obtained from the International Tables for Crystallography[31]. All calculations were performed with either SHELX76 (**1**)[32] or SHELXL93 (**5**)[33] and the PLATON package[34] (geometrical calculations and illustrations) on a DEC-5000 cluster.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).

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