[Pd(N,N-chelate)(olefin)] Complexes Containing Chiral Nitrogen Chelates Based on Carbohydrates – Enantioselectivity of Olefin Coordination

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Dedicated to Prof. Fausto Calderazzo on the occasion of his 70th birthday

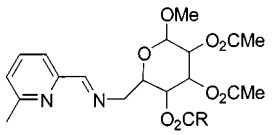
Keywords: Palladium / Bidentate nitrogen ligands / Carbohydrates / Alkenes / Enantioselectivity

Chiral N,N-chelates of formula 6-Me-pyridine–2-CH=N–R (**1**) and R–N=CH–CH=N–R (**2**) (R = 6-deoxy-α-D-glucoside or 6-deoxy-α-D-mannoside residue) and their palladium(0) complexes [Pd(N,N-chelate)(olefin)] (**I**) were prepared. Symmetrical type **2** ligands induced higher enantioselectivity in the coordination of prochiral olefins. The ability of a type **1** chelate to promote a stereoselective process was also assessed, i.e. dimethylfumarate inserted into the Pd–Me bond formed upon methylation of a type **I** complex with 50% ee. Finally, a water-soluble Pd^0 complex was also prepared by deprotecting the alcoholic functions on the sugar residue, and its molecular structure determined through X-ray diffractometry.

Introduction

An important challenge that chemical sciences must meet in the forthcoming third millenium is that of making available chiral products by means of environmentally friendly processes. Organometallic chemistry may be able to fulfill this demand,[1] since metal-assisted enantioselective syntheses can often reduce the consumption of resources. To date, the best results have been achieved by using phosphanes as chiral auxiliaries of active transition metals.[2] However, nitrogen ligands are attracting increasing interest.[3] Aiming to contribute to this growing field of research, we investigated the feasibility of using new chiral N,N-chelates based on carbohydrates[4] (Figure 1), with the assumptions that (i) these natural products can be a convenient source of chiral auxiliaries, and (ii) both a lypophylic and a hydrophilic form of the ligands can be available depending on whether or not the alcoholic functions are protected. In the latter case the environmental and economic benefits of using the ligands in aqueos media would be added.

In a previous report[5] we described type **1** and **2** ligands derived from α-D-mannose, and their alkene−Pt^0 complexes. A preliminarly investigation of the ability of the ligands to induce stereoselective coordination of prochiral olefins yielded encouraging results. Therefore, our studies have been extended to the synthesis of related chelates based on α-D-glucose. Olefin−Pd^0 species containing nitrogen ligands are currently receiving a lot of attention,[6] so [Pd(N,N-chelate)(olefin)] complexes **I** were prepared. In this paper we describe the synthesis of the ligands, and the preparation and the solution behaviour of the complexes. The ability of the chelates to induce enantioselective coordination of prochiral olefins is also discussed. Furthermore, the ability of one chelate to promote a stereoselective stoichiometric process is assessed, i.e. insertion of dimethylfumarate into the Pd−Me bond formed upon oxidative addition of Me_3OBF_4 to a complex of type **I**. Finally, preparation of a water-soluble compound of type **I** by deprotecting the alcoholic functions on the sugar residue is reported, along with its structure as determined through X-ray crystallography.



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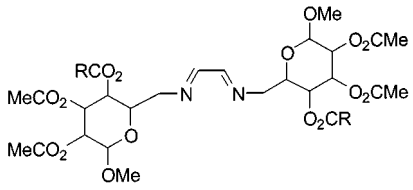

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Figure 1. General formula of type **1** and **2** ligands

[Pd(N,N-chelate)(olefin)]
I

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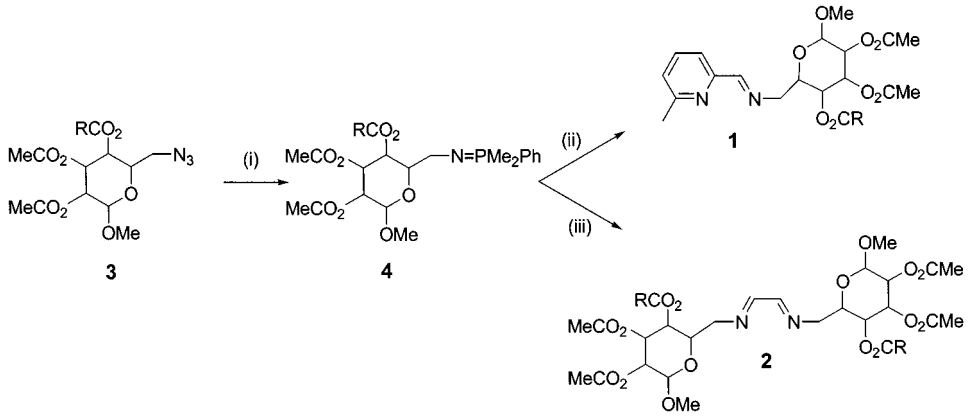
Results and Discussion

Synthesis and Characterization of the Ligands

The synthesis of the N,N-chelates is depicted in Scheme 1. The compounds are identified by a number followed by a capital letter, which indicates the sugar (M = mannose or G = glucose), and by the specification of the R substituent (Me or Ph). The symmetry of ligands of type **1** and **2** is C_1 and C_2, respectively. For both types three different derivatives were obtained. Among derivatives of type **1**, **1G-Ph** and **1M-Ph** differ by the nature of the carbohydrate (respectively glucose and mannose), substituents being equal. **1G-Me** and **1G-Ph** are both based on glucose, while the R substituent in position 4 is different. Analogous considerations hold true for ligands of type **2**.



Scheme 1

Known procedures allowed the synthesis of methyl-2,3,4-tri-*O*-acetyl-6-azido-6-deoxy-α-D-glucoside (**3G-Me**),[7] methyl-2,3-di-*O*-acetyl-4-*O*-benzoyl-6-azido-6-deoxy-α-D-glucoside (**3G-Ph**),[8][9] methyl-2,3-di-*O*-acetyl-4-*O*-benzoyl-6-azido-6-deoxy-α-D-mannoside (**3M-Ph**)[9] by starting from the corresponding commercial methyl-α-D-piranosides. Reaction of these azides with $PMePh_2$ afforded the iminophosphoranes **4**,[10] which were converted in situ into type **1** or type **2** ligands by condensation with, respectively, 6-methyl-2-pyridinecarboxaldehyde or glyoxal. The ligands were obtained in pure form as white powders by column chromatography. Their characterization was performed through NMR spectroscopy, elemental analysis and optical activity measurements (see Experimental Section).

Synthesis of [Pd(N,N-chelate)(olefin)] Complexes (I)

It is known[11] that the metal−alkene bond can be described in terms of a σ donation from the filled alkene π orbital to an empty metal orbital, and a π back donation from a filled metal orbital to the empty π* orbital of the alkene. The latter contribution plays a prominent role in Pd^0- and Pt^0-olefin complexes, and, for this reason, their stability increases as the electron-acceptor properties of the alkene grow.[6a,6d,6e]

In the presence of good donor ligands,[6e,12] such as type **1** or **2** diimines, a satisfactory electronic balance within the complex is met only if the alkene is able to withdraw effectively electron density from the metal centre through π back donation. Hence, stable type **I** complexes could be obtained only with olefins bearing good electron-acceptor substituents. Dimethylfumarate (dmf), fumarodinitrile (fdn), and maleic anhydride (ma) were effectively used. The synthesis of the complexes was performed by reacting $[Pd(dba)_2]$[13] (dba = dibenzylideneacetone) with the chelate and the olefin in dry toluene (Equation 1). The products were obtained in pure form after column chromatography as yellow to orange microcrystalline powders.

$$[Pd(dba)_2] + \text{N,N-chelate} + \text{olefin} \rightarrow \mathbf{I} + 2\ \text{dba} \quad (1)$$

Alternatively, fdn or ma derivatives could be synthetized by substituting dmf in **I** according to Equation 2.

$$[Pd(\text{N,N-chelate})(\text{dmf})] + \text{ma} \rightarrow [Pd(\text{N,N-chelate})(\text{ma})] + \text{dmf} \quad (2)$$

Only with ligands **1** was it possible to obtain dmf complexes of type **I** in acceptable yields, while in the presence of chelates **2** dmf complexes displayed little stability. These results probably reflect the electronic features of both the alkenes and the N,N-chelates. Actually, fdn and ma show similar electron-withdrawing abilities, both more pronounced than that displayed by dmf.[6d,14] Furthermore, according to previous studies,[12] ligands **2** are expected to be better σ donors than ligands **1** where one nitrogen atom belongs to a pyridine ring. Therefore, it seems reasonable that the above-mentioned good electronic balance within the complex can be achieved only in the presence of fdn or ma.

Type **I** complexes can be handled in air and were stored for long time at 233 K without appreciable decomposition.

They were fairly soluble in chlorinated solvents or toluene, but were poorly soluble in ether and insoluble in hexane. Complexes of type **1** ligands were stable in solution, while a slow decomposition process (days to completion) leading to Pd, N,N-chelate and free olefin was monitored for type **I** complexes containing ligands **2**.

NMR Spectroscopy

Large high-field shift [$\Delta\delta(^1H) \geqslant 3$ ppm, $\Delta\delta(^{13}C) \geqslant 90$ ppm] of both olefin protons and carbons was observed in the NMR spectra (Tables 1 and 2) according to a remarkable π back donation contribution to the Pd−alkene bond. As expected, the shift[15] was more pronounced for maleic anhydride and fumarodinitrile, which display the better electron-acceptor properties.

NMR spectra also allowed information to be gained on the solution behaviour of species of type **I**. Previous studies[6d,6e] disclosed that [Pd(N,N-chelate)(olefin)] complexes can be involved in dynamic processes in solution, i.e. olefin dissociation/association and olefin rotation around the metal−alkene axis. The rate of both processes decreases as the bulkiness of the N,N-ligand and/or the electron-accepting properties of the alkene grow.

For a given complex of type **I** the number of possible isomers and their symmetry depend on the geometry of both the alkene and the N,N-chelate. Prochiral olefins (dmf or fdn, C_{2h} symmetry) can afford two diastereomers depending on whether the alkene coordinates *re* or *si*. They can interconvert by dissociation of the alkene and its reassociation (with the opposite enantioface) to Pd. Spectra recorded at 298 K displayed separated signals for the diastereomers, which indicates that their interconversion, and hence olefin dissociation, is slow[16] at room temperature. At 328 K the spectra showed little difference with respect to those recorded at room temperature, but for variation of the olefin patterns due to the increased rate of alkene rotation. However, when an excess of olefin was added, the signals broadened even at room temperature. Two exceptions were [Pd(**2G-Me**)(fdn)], for which it was necessary to raise the temperature in order to observe broad olefin signals, and [Pd(**1G-Me**)(dmf)], whose spectrum at 328 K displayed averaged signals for the diastereomers even in the absence of free dmf. This spectral evidence indicates that the rate of alkene dissociation−reassociation is increased by the presence of free unsaturated ligand, according to an associative mechanism.[6d,6e]

The two halves of dmf or fdn in each one of the diastereomers containing either **1M-Ph** or **1G-Me** appeared not to be equivalent at 298 K, i.e. olefin protons gave rise to doublets or AB quartets and/or the corresponding carbons resonated separately. This result indicates that at room temperature olefin rotation is also slow, since a fast rotation would exchange the two halves of the unsaturated ligand. As expected, olefin resonances broadened in the spectra at 328 K, due to a fastened olefin rotation.

On the other hand, the room-temperature NMR spectra of [Pd(**1G-Ph**)(fdn)] showed a symmetrical olefin in one of the two diastereomers. This suggests that olefin rotation may or may not be hindered, according to which enantioface is coordinated. At 328 K olefin rotation also becomes

Table 1. Selected ^{1}H-NMR data[a] for [Pd(N,N-chelate)(olefin)] complexes

Complex	N=CH	HC=CH	6-*Me*-py	$MeCO_2$
[Pd(**1M-Ph**)(dmf)] isomer, 55%	8.32 (1 H)	3.84 (ABq, 2 H)	2.71 (3 H)	2.18 (3 H), 1.88 (3 H)
[Pd(**1M-Ph**)(dmf)] isomer, 45%	8.40 (1 H)	3.84 (ABq, 2 H)	2.73 (3 H)	2.18 (3 H), 1.88 (3 H)
[Pd(**1M-Ph**)(ma)] isomer, 60%	8.29 (1 H)	4.1−3.8 (m, 2 H)	2.66 (3 H)	2.18 (3 H), 1.88 (3 H)
[Pd(**1M-Ph**)(ma)] isomer, 40%	8.34 (1 H)	4.1−3.8 (m, 2 H)	2.68 (3 H)	2.18 (3 H), 1.89 (3 H)
[Pd(**1M-Ph**)(fdn)] isomer, 55%	8.42 (1 H)	[b,c]	2.87 (3 H)	2.18 (3 H), 1.90 (3 H)
[Pd(**1M-Ph**)(fdn)] isomer, 45%	8.30 (1 H)	[b,c]	2.67 (3 H)	2.18 (3 H), 1.87 (3 H)
[Pd(**1G-Ph**)(dmf)] isomer, 55%	8.29 (1 H)	[d]	2.71 (3 H)	2.07 (3 H), 1.90 (3 H)
[Pd(**1G-Ph**)(dmf)] isomer, 45%	8.32 (1 H)	[d]	2.72 (3 H)	2.09 (3 H), 1.90 (3 H)
[Pd(**1G-Ph**)(fdn)] isomer, 55%	8.38 (1 H)	[e,c]	2.85 (3 H)	2.09 (3 H), 1.91 (3 H)
[Pd(**1G-Ph**)(fdn)] isomer, 45%	8.29 (1 H)	[e,c]	2.63 (3 H)	2.09 (3 H), 1.88 (3 H)
[Pd(**1G-Me**)(dmf)] isomer, 55%	8.32 (1 H)	[f,c]	2.79 (3 H)	2.14 (3 H), 2.06 (3 H), 2.02 (3 H)
[Pd(**1G-Me**)(dmf)] isomer, 45%	8.27 (1 H)	[f,c]	2.82 (3 H)	2.14 (3 H), 2.05 (3 H), 2.03 (3 H)
[Pd(**1G-Me**)(fdn)] isomer, 85%	8.38 (1 H)	2.91 (2 H)	2.90 (3 H)	2.16 (3 H), 2.07 (3 H), 2.02 (3 H)
[Pd(**1G-Me**)(fdn)] isomer, 15%	8.33 (1 H)	[d]	2.90 (3 H)	2.05 (3 H), 2.02 (3 H), 1.99 (3 H)
[Pd(**2M-Ph**)(fdn)] isomer, 70%	8.06 (2 H)	2.93 (2 H)		2.16 (6 H), 1.90 (6 H)
[Pd(**2M-Ph**)(fdn)] isomer, 30%	8.03 (2 H)	2.86 (2 H)		2.15 (6 H), 1.86 (6 H)
[Pd(**2M-Ph**)(ma)]	7.92 (2 H)	3.93 (d, 1 H), 3.78 (d, 1 H)		2.18 (6 H), 1.90 (6 H)
[Pd(**2G-Ph**)(fdn)] isomer, 75%	8.05 (2 H)	2.93 (2 H)		2.08 (6 H), 1.90 (6 H)
[Pd(**2G-Ph**)(fdn)] isomer, 25%	[d]	2.86 (2 H)		2.08 (6 H), 1.87 (6 H)
[Pd(**2G-Me**)(fdn)] isomer, 97%	8.10 (2 H)	2.89 (2 H)		2.11 (6 H), 2.05 (6 H), 2.01 (6 H)
[Pd(**1M***)(fdn)] isomer, 55%[g]	8.74 (1 H)	[h]	2.88 (3 H)	
[Pd(**1M***)(fdn)] isomer, 45%[g]	8.71 (1 H)	[h]	2.91 (3 H)	

[a] At 298 K and 250 MHz. In $CDCl_3$, $CHCl_3$ (δ = 7.26) as internal standard. The following abbreviations are used for describing NMR multiplicities: app, apparent; no attribute, singlet; d, doublet; ABq, AB quartet; m, multiplet. − [b] The olefin protons resonate at δ = 2.91 (ABq, 2 H) and 2.89 (app d, 2 H). − [c] Due to the similar abundance of the diastereomers the signals cannot be attributed unequivocally. − [d] Hidden by other signals. − [e] The olefin protons resonate at δ = 2.87 (2 H) and 2.91 (ABq, 2 H). − [f] The olefin protons resonate at δ = 3.82 (2 H) and 3.63 (m, 2 H). − [g] In D_2O, HDO (δ = 4.80) as internal standard. − [h] The olefin protons resonate at δ = 3.24 (app d, 2 H) and 3.18 (ABq, 2 H).

Table 2. Selected ^{13}C-NMR data[a] for [Pd(N,N-chelate)(olefin)] complexes

Complex	N=CH	OCH(OMe)	NCH_2	HC=CH
[Pd(**1M-Ph**)(dmf)] isomer, 55%	165.2 (1 C)	98.3 (1 C)	64.9 (1 C)	41.6 (1 C), 41.3 (1 C)
[Pd(**1M-Ph**)(dmf)] isomer, 45%	165.4 (1 C)	98.5 (1 C)	63.9 (1 C)	42.1 (1 C), 41.2 (1 C)
[Pd(**1M-Ph**)(ma)] isomer, 60%	165.4 (1 C)	98.5 (1 C)	64.9 (1 C)	[b,c]
[Pd(**1M-Ph**)(ma)] isomer, 40%	165.6 (1 C)	98.6 (1 C)	64.1 (1 C)	[b,c]
[Pd(**1M-Ph**)(fdn)] isomer, 55%	165.7 (1 C)	98.5 (1 C)	63.4 (1 C)	[d,c]
[Pd(**1M-Ph**)(fdn)] isomer, 45%	165.3 (1 C)	98.8 (1 C)	65.1 (1 C)	[d,c]
[Pd(**1G-Ph**)(dmf)] isomer, 55%	170.4 (1 C)	96.3 (1 C)	64.8 (1 C)	[e,c]
[Pd(**1G-Ph**)(dmf)] isomer, 45%	170.4 (1 C)	96.3 (1 C)	63.9 (1 C)	[e,c]
[Pd(**1G-Ph**)(fdn)] isomer, 55%	165.8 (1 C)	96.8 (1 C)	63.2 (1 C)	[f,c]
[Pd(**1G-Ph**)(fdn)] isomer, 45%	165.4 (1 C)	96.7 (1 C)	65.0 (1 C)	[f,c]
[Pd(**1G-Me**)(dmf)] isomer, 55%	162.3 (1 C)	96.4 (1 C)	63.0 (1 C)	42.0 (1 C), 41.5 (1 C)
[Pd(**1G-Me**)(dmf)] isomer, 45%	165.4 (1 C)	96.0 (1 C)	64.4 (1 C)	42.4 (1 C), 41.2 (1 C)
[Pd(**1G-Me**)(fdn)] isomer, 85%	165.5 (1 C)	96.5 (1 C)	62.9 (1 C)	18.4 (1 C), 18.2 (1 C)
[Pd(**2M-Ph**)(fdn)] isomer, 70%	161.5 (2 C)	98.7 (2 C)	63.3 (2 C)	19.4 (2 C)
[Pd(**2M-Ph**)(fdn)] isomer, 30%	160.4 (2 C)	98.5 (2 C)	64.7 (2 C)	19.1 (2 C)
[Pd(**2M-Ph**)(ma)]	161.3 (2 C)	98.6 (1 C), 98.4 (1 C)	65.0 (1 C), 63.9 (1 C)	42.4 (1 C), 42.0 (1 C)
[Pd(**2G-Ph**)(fdn)] isomer, 75%	161.7 (2 C)	96.8 (2 C)	63.4 (2 C)	19.5 (2 C)
[Pd(**2G-Ph**)(fdn)] isomer, 25%	160.5 (2 C)	96.7 (2 C)	64.6 (2 C)	19.2 (2 C)
[Pd(**2G-Me**)(fdn)] isomer, 97%	161.6 (2 C)	96.6 (2 C)	63.4 (2 C)	19.4 (2 C)
[Pd(**1M***)(fdn)] isomer, 55%	161.5 (1 C)	101.1 (1 C)	63.3 (1 C)	[g,c]
[Pd(**1M***)(fdn)] isomer, 45%	161.5 (1 C)	100.7 (1 C)	64.7 (1 C)	[g,c]

[a] At 298 K and 62.9 MHz. In $CDCl_3$, $^{13}CDCl_3$ (δ = 77.0) as internal standard. – [b] The olefin carbon atoms resonate at δ = 41.4 (1 C), 41.0 (2 C), 40.7 (1 C). – [c] Due to the similar abundance of the diastereomers the signals cannot be attributed unequivocally. – [d] The olefin carbon atoms resonate at δ = 18.3 (3 C), 17.7 (1 C). – [e] The olefin carbon atoms resonate at δ = 42.1 (1 C), 41.6 (1 C), 41.2 (2 C). – [f] The olefin carbon atoms resonate at δ = 18.3 (2 C), 18.1 (1 C), 17.6 (1 C). – [g] The olefin carbon atoms resonate at δ = 17.4 (3 C), 17.1 (1 C).

fast in the more stereochemically rigid isomer. A similar situation holds true for [Pd(**1G-Ph**)(dmf)].

No information concerning olefin rotation was available from NMR spectra of dmf or fdn derivatives containing ligands of type **2**. Actually, since the complexes display C_2 symmetry, all the nuclei related by the twofold axis are expected to be equivalent.

Maleic anhydride (C_{2v} symmetry) affords complex [Pd(**1M-Ph**)(ma)] in two isomeric forms, which can interconvert by either olefin rotation or dissociation/reassociation of the alkene. Since the isomers are separately observed in both spectra, it can be inferred that both motions are hindered at room temperature. At 328 K the proton spectrum consists of a unique broad pattern due to fast interconversion of the diastereomers. Conversely, complex [Pd(**2M-Ph**)(ma)] exists as a unique isomer. Both ^{1}H- and ^{13}C-NMR spectra show an unsymmetrical olefin, thus demonstrating that dissociation/reassociation of the alkene is slow at 298 K. Also the rotation of the alkene is hindered at room temperature, as suggested by the nonequivalence of the two halves of the N,N-ligand in the carbon spectrum. On raising the temperature to 328 K olefin rotation becomes fast, as suggested by the presence of a symmetric and sharp proton pattern for the N,N-chelate.

Enantioselectivity of Olefin Coordination

As mentioned above, the coordination of prochiral olefins to the [Pd(N,N-chelate)] moiety gives rise to two diastereomers according to which enanantioface is bound to the metal centre. Fresh solutions of complexes of type **I** displayed the presence of both diastereomers, whose ratio could be measured by integrating suitable peaks (Table 3). The ratio was neither affected by prolonged standing in solution nor by the presence of free olefin, which merely increased the rate of interconversion of the diastereomers (see above). These observations indicate that equilibrium is reached within a few seconds from dissolution of the samples. Analogous platinum compounds[5] require several minutes before equilibrium is attained.

Table 3. Diastereomeric equilibrium composition[a] for complexes of type **I** with prochiral olefins

Complex	Composition
[Pd(**1M-Ph**)(dmf)]	55:45
[Pd(**1M-Ph**)(fdn)]	55:45
[Pd(**1G-Ph**)(dmf)]	55:45
[Pd(**1G-Ph**)(fdn)]	55:45
[Pd(**1G-Me**)(dmf)]	55:45
[Pd(**1G-Me**)(fdn)]	85:15
[Pd(**2M-Ph**)(fdn)]	70:30
[Pd(**2G-Ph**)(fdn)]	75:25
[Pd(**2G-Me**)(fdn)]	97:3
[Pd(**1M***)(fdn)][b]	55:45

[a] In $CDCl_3$ at 298 K. – [b] In D_2O at 298 K.

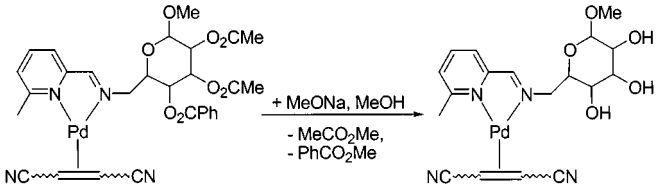
An inspection of Table 3 reveals that the most relevant result concerning enantioselectivity was obtained in the case of [Pd(**2G-Me**)(fdn)]. The ratio between the diastereomers was estimated to be 97:3, indicating a strong preference for the coordination of one enantioface. Discrimination was also observed for the same olefin in the presence of either **2G-Ph** or **2M-Ph**, although to a lesser extent, affording diastereomeric ratios of 75:25 and 70:30, respectively. These results reveal that changing the 4-substituent on the glucoside residue (**2G-Me** vs **2G-Ph**) plays a more important role

than variation of the carbohydrate residue itself (**2G-Ph** vs **2M-Ph**). Among ligands **1**, only **1G-Me** competes with the symmetrical chelates, giving rise to a diastereomeric ratio of 85:15 in the presence of fdn. Conversely, the other ligands of type **1** induce little preference for one enantioface of dmf or fdn. It is also noteworthy that the values of diastereomeric excesses reported in Table 3 are very close to those measured for corresponding Pt^0 complexes containing the same ligands,[5][17] as observed for other related M^0 compounds.[6e,18]

These findings indicate that type **2** ligands prompt more effectively enantioselective coordination of *trans*-olefins. It is also observed that **1G-Me** and **2G-Me**, both based on a glucoside having acetyl groups as substituents, display the better discriminating properties within the corresponding class. However, the complexity of the ligands in terms of both steric and electronic features does not allow an easy rationalization of the factors which determine these results.

Synthesis and X-ray Structure of the Water-Soluble Complex [Pd(1M*)(fdn)]

Water-soluble Pd^0 complexes have recently attracted attention due to their possible use as catalysts in aqueous media.[19] During this work we successfully attempted the synthesis of a water-soluble type **I** complex by deprotecting the alcoholic functions in the sugar residue of the ligand. Treatment of [Pd(**1M-Ph**)(fdn)] with a catalytic amount of sodium methoxide in methanol resulted in quantitative hydrolysis of the ester groups of the carbohydrate residue (Scheme 2).



Scheme 2

The corresponding product [Pd(**1M***)(fdn)] could be isolated in high yield by adding diethyl ether to the reaction mixture. The most prominent feature of the complex is its solubility in both lypophilic (e.g. chloroform) and hydrophylic (e.g. water or methanol) solvents. Analogous to its parent derivative, the complex exists in solution as an equilibrium mixture of two diastereomers in 55:45 ratio.

The X-ray solid-state structure of the complex was determined. Crystallization from methanol/diethyl ether yielded

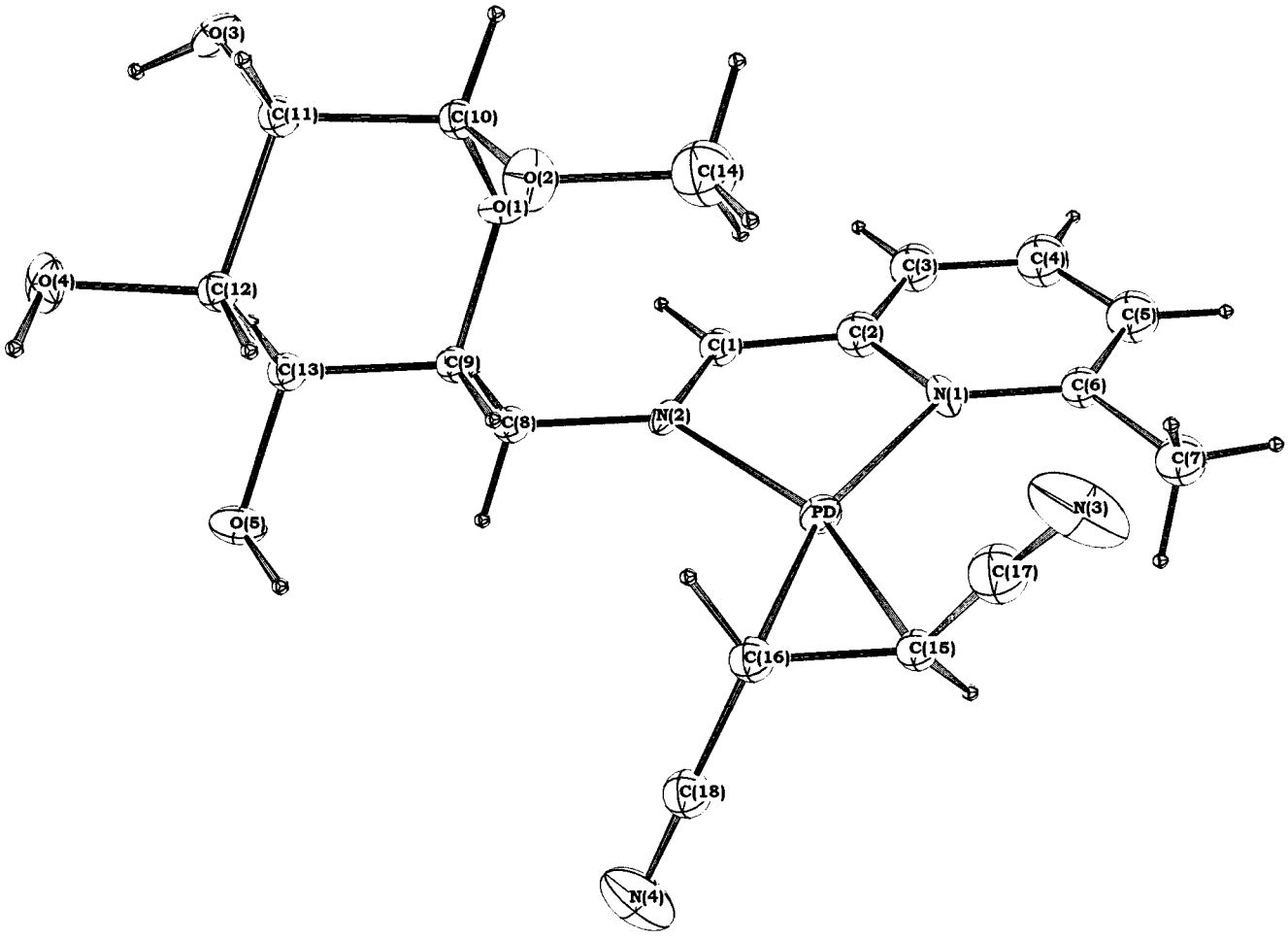


Figure 2. ORTEP view of [Pd(**1M***)fdn] showing the atom labelling scheme

single crystals only for one of the two diastereomers. An ORTEP drawing of this molecule with the atom labelling scheme is shown in Figure 2. Relevant geometric parameters are given in Table 4.

Table 4. Selected geometrical parameters for [Pd(**1M***)-(fdn)]·MeOH[a]

Bond lengths [Å]	
Pd−N(2)	2.11(1)
Pd−N(1)	2.17(1)
Pd−C(15)	2.05(2)
Pd−C(16)	2.04(2)
C(15)−C(17)	1.38(3)
C(15)−C(16)	1.46(3)
C(1)−C(2)	1.43(2)
C(17)−N(3)	1.19(3)
C(16)−C(18)	1.40(3)
N(1)−C(2)	1.37(2)
C(18)−N(4)	1.17(3)
N(2)−C(1)	1.27(2)
N(1)−C(6)	1.34(2)
C(8)−C(9)	1.53(2)
N(2)−C(8)	1.46(2)
Bond angles [°]	
N(1)−Pd−N(2)	77.5(5)
C(15)−Pd−C(16)	41.8(7)
N(1)−Pd−C(15)	122.3(6)
N(2)−Pd−C(16)	118.3(6)
Pd−C(15)−C(16)	69(1)
Pd−C(16)−C(15)	69(1)
C(16)−C(15)−C(17)	113(2)
C(15)−C(16)−C(18)	114(2)
N(3)−C(17)−C(15)	173(3)
N(4)−C(18)−C(16)	179(2)
Pd−N(1)−C(2)	112(1)
Pd−N(2)−C(1)	114(1)
N(2)−C(1)−C(2)	122(1)
Pd−N(2)−C(8)	126(1)
C(1)−N(2)−C(8)	120(1)
N(2)−C(8)−C(9)	110(1)
Torsional angles [°]	
Pd−C(16)−C(15)−C(17)	110(1)
Pd−C(15)−C(16)−C(18)	105(1)
Pd−N(2)−C(8)−C(9)	56(2)
N(2)−C(8)−C(9)−O(1)	62(1)
C(17)−C(15)−C(16)−C(18)	−145(2)

[a] ESDs in parentheses.

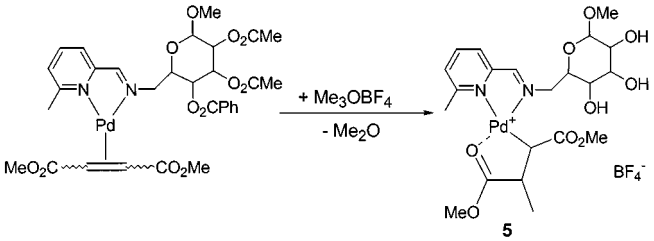
As expected[6e] for zerovalent [Pd(N,N-chelate)(olefin)] complexes the coordination geometry at Pd is trigonal planar. The coordination plane includes the pyridine ring. In fact, the atoms Pd, N(1), N(2), C(15), C(16), C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(8) are coplanar within 0.06(2) Å. The sugar residue adopts the expected chair conformation and its mean plane is almost orthogonal to the coordination plane. As a consequence of the chemical non-equivalence, the bond lengths Pd−N(1) [2.17(1) Å] and Pd−N(2) [2.11(1) Å] are slightly, but significantly, different, and lie at the extremes of the range commonly found in Pd/α-diimine complexes,[6a,6c,6e] the shorter bond being adjacent to the double bond C(1)−N(2). The bite angle N(1)−Pd−N(2) [77.5(5)°] is very close to that found for most bidentate nitrogen ligands.[6c,6e] The olefin is bound to the metal in a regular arrangement. The two Pd−C bond lengths are equal, within the experimental error [average value 2.045(20) Å], and compare well with the values found in Pd complexes of α-diimines with electron-poor olefins.[6c,6e] The lengthening of the olefinic bond [C(15)−C(16) 1.46(3) Å], and the large out-of-plane displacements of the cyano groups [the torsion angle C(17)−C(15)−C(16)−C(18) being 145(2)°] compared with the value of 1.34 Å for the free alkene provide clear evidence of a rehybridization towards sp^3 of the olefinic carbon atoms upon coordination, in keeping with the substantial π back donation from the metal (see above).

Addition of Me_3OBF_4 to [Pd(1G-Ph)(dmf)]

Use in catalysis of type **I** complexes seems plausible.[6f] As organic processes promoted by Pd^0 species often involve oxidative addition to Pd^{II} and/or (stereoselective) insertion of unsaturated substrates into Pd^{II}−alkyl bonds, a preliminarly investigation of the feasibility of stoichiometric reactions of this kind in the coordination environment provided by a chelate of type **1** was made.

We previously reported[20] that [Pd(1,10-phen)(dmf)] reacts with Me_3OBF_4 affording the cyclometallated Pd^{II} product [Pd{CH(CO_2Me)CHMe(CO^aOMe)}(1,10-phen)-(*Pd*−O^a)]BF_4. The process proceeds in two steps, i.e. (i) oxidative addition of the oxonium salt to the Pd^0 complex affording the Pd^{II}−Me bond, and (ii) olefin insertion with attainment of a stereogenic carbon atom bound to Pd.

The analogous reaction was performed on [Pd(**1G-Ph**)(dmf)] (Scheme 3). The process was monitored through NMR spectroscopy and was complete within 24 hours at room temperature affording **5**. The *trans* arrangement of the carbonyl group with respect to the *N*-imino atom was assigned, taking into account the well-established geometry of a closely related Pt^{II} species.[5] The presence of two diastereomers in 75:25 ratio indicates that the reaction had occurred with significant stereoselectivity.



Scheme 3

Conclusion

This work demonstrated the reasonable feasibility of synthesising chiral diimino ligands based on carbohydrates. Results of preliminary investigations into their ability in inducing enantioselective processes were promising results, with Pd^0 complexes with prochiral olefins being prepared

stereoselectively and achievement of a stoichiometric asymmetric insertion process. A rare example of a chiral Pd^0 water-soluble complex was also provided by deprotecting the alcoholic groups of the carbohydrate residue in one ligand, and its structure determined through X-ray diffractometry.

Experimental Section

General: NMR spectra were recorded with a 250-MHz spectrometer (Bruker Model AC-250). The solvents were $CDCl_3$ [$CHCl_3$ (δ = 7.26) and $CDCl_3$ (δ = 77.0) as standards for ^1H and ^{13}C spectra, respectively] and CD_3NO_2 [CD_2HNO_2 (δ = 4.33) and $^{13}CD_2HNO_2$ (d = 62.9) as standards for ^1H and ^{13}C spectra, respectively]. Optical activity measurements were performed with a Perkin−Elmer Polarimeter (Model 141). The following abbreviations are used for describing NMR multiplicities: d, doublet; dd, double doublet; dt, double triplet; m, multiplet; no attribute, singlet; t, triplet. − Compounds **3G-Me**,[7] methyl-2,3-di-*O*-acetyl-4-*O*-benzoyl-6-bromo-6-deoxy-α-D-glucoside,[8] **1M-Ph**,[5] **2M-Ph**[5] and $[Pd(dba)_2]$[13] were prepared according to published methods. Toluene was distilled from sodium, dichloromethane from calcium hydride, and methanol from magnesium immediately before use. − Elemental analysis for the new compounds are collected in Table 5.

3G-Ph: The compound was prepared in 80% yield as described for **3M-Ph**[9] by starting from methyl-2,3-di-*O*-acetyl-4-*O*-benzoyl-6-bromo-6-deoxy-α-D-glucoside.[8] − ^1H-NMR resonances (in $CDCl_3$, at 250 MHz): δ = 7.97 (d, 2 H), 7.57 (t, 1 H), 7.45 (t, 2 H), 5.68 (t, 1 H), 5.22 (t, 1 H), 5.02 (d, 1 H), 4.95 (dd, 1 H), 4.08 (m, 1 H), 3.48 (3 H, OMe), 3.40 (m, 2 H), 2.09 (3 H, $MeCO_2$), 1.89 (3 H, $MeCO_2$). − Selected ^{13}C-NMR resonances (in $CDCl_3$, at 62.9 MHz): δ = 96.7 (1 C, C1 of glucoside), 70.9, 70.2, 69. 4, 68.9 (4 C, C2−C5 of glucoside), 55.6 (1 C, OMe), 51.1 (1 C, NCH_2), 20.7 (1 C, *Me*CO_2), 20.6 (1 C, *Me*CO_2).

1G-Ph, 1G-Me, 2G-Ph, and 2G-Me: To a stirred solution of $PPhMe_2$ (0.14 g, 1.0 mmol) in 5 mL of dry dichloromethane kept in an ice bath was added dropwise a solution of the appropriate azide **3** (1.0 mmol) in 5 mL of dry dichloromethane. After the addition was complete, the ice bath was removed and formation of nitrogen was observed. Progression of the reaction was monitored by TLC analysis on silica of the reacting mixture with ethyl acetate/petroleum ether, 1:1. The reaction affording the corresponding imino-phosphorane **4** was complete within 3 hours. In the case of **1G-Ph** and **1G-Me** the solvent was removed under vacuum and the residue was dissolved in 5 mL of dry toluene containing 4-Å molecular sieves. To the solution was added 6-methyl-2-pyridinecarboxaldehyde (0.12 g, 1.0 mmol), and after 1 h of stirring at 363 K the solvent was removed under vacuum. In the case of **2G-Ph** and **2G-Me**, after formation of **4** was complete, glyoxal (40% w/w in water, 0.5 mmol) was added to the dichloromethane solution, followed by sodium sulphate. After 15 minutes the reaction mixture was filtered and the solvent removed under vacuum. In all cases, the crude reaction products were filtered through a column of Florisil (15 × 1.5 cm) with ethyl acetate/petroleum ether, 1:1 to give the products as white glassy solids (yield: 60−70%). − Selected ^1H-NMR resonances (in $CDCl_3$, at 250 MHz): **1G-Ph**: δ = 8.32 (1 H, CH=N), 5.75 (t, 1 H), 5.35 (t, 1 H), 5.00 (m, 1 H), 4.93 (1 H), 4.29 (m, 1 H), 3.90 (d, 1 H), 3.75 (dd, 1 H), 3.36 (3 H, OMe), 2.55 (3 H, Me-py), 2.07 (3 H, $MeCO_2$), 1.90 (3 H, $MeCO_2$); **1G-Me**: δ = 8.32 (1 H, CH=N), 5.50 (m, 1 H), 5.10 (t, 1 H), 4.88 (m, 2 H), 4.15 (m, 1 H), 3.84 (d, 1 H), 3.66 (dd, 1 H), 3.33 (3 H, OMe), 2.56 (3 H, Me-py), 2.05 (3 H, $MeCO_2$), 2.02 (3 H, $MeCO_2$), 2.00 (3 H, $MeCO_2$); **2G-Ph**: δ = 7.78 (2 H, CH=N), 5.70 (t, 2 H), 5.27 (t, 2 H), 4.95 (m, 4 H), 4.23 (m, 2 H), 3.77 (dd, 2 H), 3.59 (dd, 2 H), 3.40 (6 H, OMe), 2.08 (6 H, $MeCO_2$), 1.89 (6 H, $MeCO_2$); **2G-Me**: δ = 7.88 (2 H, CH=N), 5.47 (t, 2 H), 5.05 (t, 2 H), 4.87 (m, 4 H), 4.08 (m, 2 H), 3.75 (dd, 2 H), 3.57 (dd, 2 H), 3.35 (6 H, OMe), 2.05 (6 H, $MeCO_2$), 2.01 (6 H, $MeCO_2$), 1.98 (6 H, $MeCO_2$). − Selected ^{13}C-NMR resonances (in $CDCl_3$, at 62.9 MHz): **1G-Ph**: δ = 164.8 (1 C, CH=N), 96.4 (1 C, C1 of glucoside), 71.1, 71.0, 70.0 and 68.4 (4 C, C2-C5 of glucoside), 61.2 (1 C, NCH_2), 55.1 (1 C, OMe), 24.2 (1 C, *Me*-py), 20.7 (1 C, *Me*CO_2), 20.6 (1 C, *Me*CO_2); **1G-Me**: δ = 164.9 (1 C, CH=N), 96.4 (1 C, C1 of glucoside), 71.0, 70.4 and 68.1 (4 C, C2-C5 of glucoside), 60.9 (1 C, NCH_2), 55.1 (1 C, OMe), 24.1 (1 C, *Me*-py), 20.7 (3 C, *Me*CO_2); **2G-Ph**: δ = 164.2 (2 C, CH=N), 96.6 (2 C, C1 of glucosides), 71.1, 70.9, 69.9, 68.3 (8C, C2-C5 of glucosides), 61.2 (2 C, NCH_2), 55.3 (2 C, OMe), 20.8 (2 C, *Me*CO_2), 20.6 (2 C, *Me*CO_2); **2G-Me**: δ = 164.3 (2 C, CH=N), 96.5 (2 C, C1 of glucosides), 70.9, 70.3, 67.9 (8C, C2-C5 of glucosides), 60.8 (2 C, NCH_2), 55.2 (2 C, OMe), 20.7 (6 C, *Me*CO_2). − $[\alpha]_D^{25}$ (0.050 M in dichloromethane): **1G-Ph**: +100; **1G-Me**: +100; **2G-Ph**: +85; **2G-Me**: +110.

[Pd(N,N-chelate)(olefin)]: To a suspension of $[Pd(dba)_2]$ (0.58 g, 1.0 mmol) in 5 mL of dry toluene were added the N,N-chelate (1.5 mmol) and the olefin (1.5 mmol). After 1 h of stirring (12 h when olefin = dmf) the solvent was removed under vacuum from the resulting mixture. The residue was separated by chromatography on silica gel with dichloromethane (to remove dba) and then

Table 5. Elemental analyses for all new compounds

Compound	Formula	C found (calcd.)	H found (calcd.)	N found (calcd.)
1G-Me	$C_{20}H_{26}N_2O_8$	56.59 (56.87)	6.31 (6.20)	6.55 (6.63)
1G-Ph	$C_{25}H_{28}N_2O_8$	62.21 (61.98)	5.89 (5.82)	5.93 (5.78)
2G-Me	$C_{28}H_{40}N_2O_{16}$	50.87 (50.91)	6.22 (6.10)	4.32 (4.24)
2G-Ph	$C_{38}H_{44}N_2O_{16}$	57.98 (58.16)	5.59 (5.65)	3.51 (3.57)
[Pd(**1M-Ph**)(dmf)]	$C_{31}H_{36}N_2O_{12}Pd$	50.85 (50.66)	4.87 (4.94)	3.93 (3.81)
[Pd(**1M-Ph**)(ma)]	$C_{29}H_{30}N_2O_{11}Pd$	50.89 (50.56)	4.44 (4.39)	4.10 (4.07)
[Pd(**1M-Ph**)(fdn)]	$C_{29}H_{30}N_4O_8Pd$	51.90 (52.07)	4.41 (4.52)	8.30 (8.37)
[Pd(**1G-Ph**)(dmf)]	$C_{31}H_{36}N_2O_{12}Pd$	50.62 (50.66)	5.05 (4.94)	3.65 (3.81)
[Pd(**1G-Ph**)(fdn)]	$C_{29}H_{30}N_4O_8Pd$	52.23 (52.07)	4.43 (4.52)	8.61 (8.37)
[Pd(**1G-Me**)(dmf)]	$C_{26}H_{34}N_2O_{12}Pd$	46.24 (46.40)	5.21 (5.09)	4.27 (4.16)
[Pd(**1G-Me**)(fdn)]	$C_{24}H_{28}N_4O_8Pd$	47.63 (47.50)	4.60 (4.65)	9.04 (9.23)
[Pd(**2M-Ph**)(fdn)]	$C_{42}H_{46}N_4O_{16}Pd$	51.88 (52.05)	4.86 (4.78)	5.65 (5.78)
[Pd(**2M-Ph**)(ma)]	$C_{42}H_{46}N_2O_{19}Pd$	50.91 (51.00)	4.60 (4.69)	2.89 (2.83)
[Pd(**2G-Ph**)(fdn)]	$C_{42}H_{46}N_4O_{16}Pd$	52.28 (52.05)	4.66 (4.78)	5.86 (5.78)
[Pd(**2G-Me**)(fdn)]	$C_{32}H_{42}N_4O_{16}Pd$	45.60 (45.48)	5.08 (5.01)	6.81 (6.63)

with dichloromethane/methanol, 40:1. The solvents were removed under vacuum from the collected yellow-orange fractions affording the product as a yellow microcrystalline solid (yield: 75−85%). Alternatively, fdn or ma complexes could be prepared by starting from the corresponding dmf complexes, according to the following example: To a solution of [Pd(**1M-Ph**)(dmf)] (0.074 g, 0.10 mmol) in 1 mL of dichloromethane was added fumarodinitrile (0.012 g, 0.15 mmol). The resulting solution was chromatographed as described above affording pure [Pd(**1M-Ph**)(fdn)] (yield 80−85%).

[Pd(1M*)(fdn)]: To a stirred solution of [Pd(**1M-Ph**)(fdn)] (0.067 g, 0.10 mmol) in 2.5 mL of dry methanol was added a catalytic amount of sodium methoxide in the same solvent. After 30 min of reaction, separation of the yellow product was observed. After a further 16 h of stirring, the precipitation of the product was enhanced by addtion of diethyl ether. The complex was separated, washed with diethyl ether (3 × 3 mL) and dried under vacuum (0.040 g, yield: 83%).

Addition of Me_3OBF_4 to [Pd(1G-Ph)(dmf)] with Formation of 5: A solution of the complex (0.022 g, 0.030 mmol) in 0.5 mL of deuterionitromethane was added to solid Me_3OBF_4 (0.005 g, 0.033 mmol). The resulting solution was transferred into an NMR tube and spectra were recorded until no more chemical changes were detected. − Selected ^{1}H-NMR resonances (in CD_3NO_2, at 250 MHz): **5** (diastereomer, 75%): δ = 8.41 (1 H, CH=N), 4.09 (3 H, OMe), 3.50 (3 H, OMe), 3.40 (3 H, OMe), 2.70 (3 H, *Me*-py), 1.07 (d, 3 H, CH*Me*); (diastereomer, 25%): 8.42 (1 H, CH=N), 4.10 (3 H, OMe), 2.62 (3 H, *Me*-py), 1.00 (d, 3 H, CH*Me*).

X-ray Crystal-Structure Determination of [Pd(1M*)(fdn)]: Crystals suitable for X-ray analysis were grown from methanol/diethyl ether. The crystal, collection, and refinement data are presented in Table 6. Data collection was performed at room temperature with an Enraf−Nonius MACH3 diffractometer with graphite-monochromated Mo-K_α radiation using the ω/θ scan technique. The unit-cell parameters and orientation matrix were obtained from a least-squares fitting of the setting values of 25 strong reflections in the range $13° \leq \theta \leq 14°$. Three monitoring reflections, measured every 500, showed no intensity decrease. Corrections for Lorentz-polarization effects were applied but not for absorption. The structure was solved by routinary application of Patterson and Fourier techniques. Refinement on *F* was carried out by full-matrix least squares minimizing the quantity $\Sigma w(\Delta F)^2$ with $w^{-1} = [\sigma^2(F_o) + (0.02F_o)^2 + 1]$, where σ is derived from counting statistics. Owing to the insufficient number of observed reflections of high values of θ, the final refinement was carried out with anisotropic thermal parameters for Pd, O and N, and isotropic for C and the non-hydrogen atoms of the solvent molecule MeOH. H atoms at calculated positions were added as riding atoms with isotropic thermal parameters 1.3 times larger than that of the carrier atoms. The H atoms of the solvent molecule were neglected. The final Fourier difference map was within ±0.6 e/Å^3. All calculations were performed with the Enraf−Nonius (SDP) set of programs.[21] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-133171. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 6. Crystallographic data for [Pd(**1M***)(fdn)] · MeOH

Crystal size [mm]	0.02 × 0.20 × 0.30
Empirical formula	$C_{18}H_{22}N_4O_5Pd{\cdot}CH_3OH$
Molecular mass	512.8
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a [Å]	7.8370 (1)
b [Å]	27.5000 (3)
c [Å]	10.3280 (2)
V [Å^3]	2225.8
Z	4
F(000)	1048
$D_{calcd.}$ [gcm^{-3}]	1.53
$D_{measd.}$ [gcm^{-3}]	1.50
λ (Mo-K_α) [Å]	0.71073
θ_{max} [°]	27
μ [cm^{-1}]	8.61
No. of reflections measured	2837
No. of independent reflections	2774
No. of reflections above 3σ(*I*)	1167
No. of refined parameters	171
Goodness of fit	1.10
R	0.048
Rw	0.053

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