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$[Pd^0(N,N\text{-chelate})(olefin)]$ complexes containing nitrogen chelates derived from carbohydrates and their use in mild hydrogenation of olefins in water †

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New nitrogen chelates of formula $6\text{-R-C}_5H_3NCH{=}NR'\text{-}2$ and $R'N{=}CHCH{=}NR'$ (R = H or Me; R′ = 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose residue) were prepared. The nitrogen donor atom is directly linked to a chiral carbon, *i.e.* the C1 atom of the sugar ring. The ability of the ligands to induce enantioselective co-ordination of prochiral olefins was assessed by preparing palladium(0) complexes of formula [Pd(N,N-chelate)(olefin)]. Hydrophilic complexes obtained by deprotection of the hydroxy groups of the sugar residue were used for hydrogenating alkenes in water. The course of the reaction is strongly influenced by pH, and homogeneous hydrogenation of the double bond takes place only under basic conditions.

The design of new ligands for organic synthesis is an open challenge.[1] The main question connected with this field of research is the introduction of appropriate functions in a ligand backbone, which often involves synthetic difficulties and consumption of resources. These obstacles can effectively be by-passed if suitable auxiliaries are chosen among the plenty of naturally occurring compounds. The simplest carbohydrates are good candidates as they are easily available, chiral, and may afford both lipo- and hydro-soluble ligands[2] depending on whether or not the hydroxyl groups are protected. Furthermore, the impressive literature on carbohydrates[3] describes several straightforward procedures for their derivatization.

On these grounds, we recently prepared new nitrogen chelates (**1**, **1M*** and **2** in Fig. 1) based on α-D-mannose and α-D-glucose,[4] where the sugar residue was bound to the N-donor through the C6 atom. Their co-ordination properties were investigated by preparing lypo- and hydro-soluble complexes of Pd^0 and Pt^0 with general formula $[M^0(N,N\text{-chelate})(olefin)]$. A significant diastereoselectivity in the co-ordination of both dimethyl fumarate and fumarodinitrile (fdn) was obtained only with ligands of type **2**, while it was found that chelates of type **1** induced poor enantioselectivity.[5] This result can reasonably be ascribed to the distance of the chiral auxiliary from the metal center, which may not allow the chiral information to be effectively transferred to the metal co-ordination sphere.

Thus, we were stimulated to prepare new N,N-ligands with a chiral carbon closer to the co-ordinating atoms, *i.e.* by establishing a linkage between the carbohydrate C1 carbon and the N donor. In this report we describe the successful approach to the synthesis of the new ligands **3**, **4** and **5** (Fig. 1), and their palladium(0) complexes [Pd(N,N-chelate)(olefin)] **I**. The availability of the hydrophilic form of the ligands prompted us to contribute to the flourishing chemistry in aqueous media.[2a,h,i,6] Beside safety advantages, water soluble catalysts offer the possibility of extracting the products with an organic solvent, while the active water phase can be recycled for further reaction. Thus, a new water soluble compound was prepared by hydrolysis of the acetyl groups in [Pd(**3**)(fdn)]. The resulting complex and the previously described [Pd(**1M***)(fdn)][4a] were successfully tested as catalysts in the hydrogenation of olefins in water. The dependence of the performance of the catalysts on the pH was also investigated.

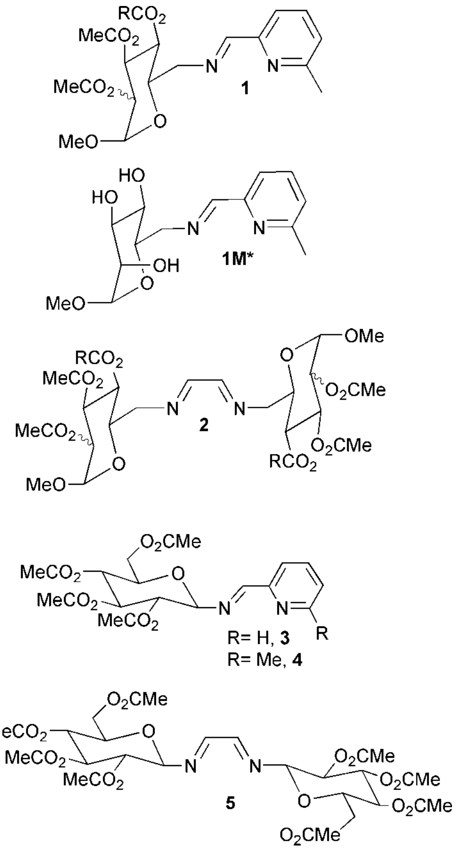

Fig. 1 Ligands of types **1**–**5**; M = mannose.

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† Dedicated to Professor Paolo Corradini on the occasion of his 70th birthday.

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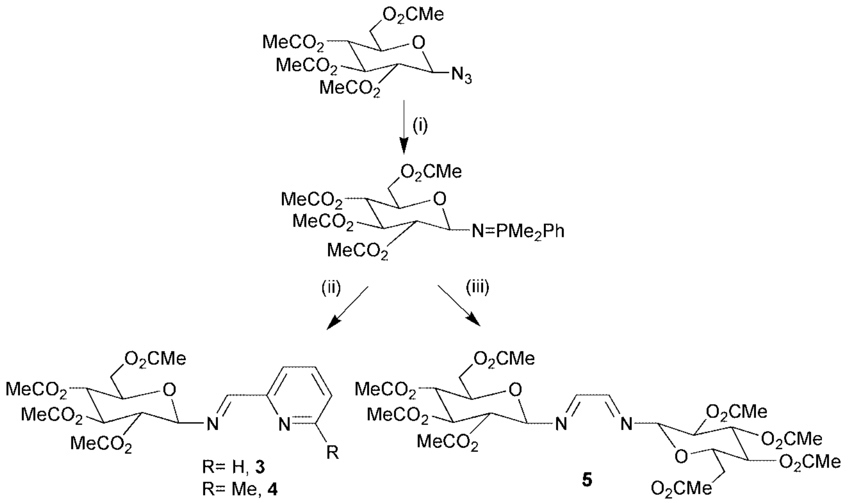


Scheme 1 (i) $+PMe_2Ph$, $-N_2$; (ii) $+6\text{-R-}C_5H_3NCHO\text{-}2$, $-O{=}PMe_2Ph$; (iii) +0.5 OHCCHO, $-O{=}PMe_2Ph$.

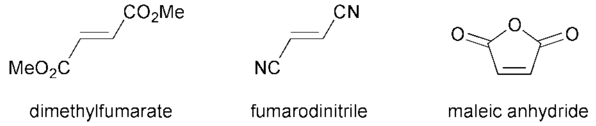


Fig. 2 Olefins used in the synthesis of complexes of type **I**.

Results and discussion

Synthesis of compounds 3, 4 and 5 and of their [Pd(N,N-chelate)(olefin)] complexes

All the ligands display a 1,3-diimine skeleton with 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose residues bound to the N atoms through the C1 carbon atom. More precisely, both nitrogens in **5** (C_2 symmetry) are linked to a sugar moiety, while **3** and **4**, where one nitrogen belongs to a pyridine unit, display lower symmetry (C_1). The latter two chelates differ in the presence of H or Me, respectively, in position 6 of the heteroaromatic ring.

The ligands were synthesized by adapting the procedure previously used[4a] for preparing chelates of type **1** and **2** (Scheme 1). This involves attainment of an iminophosporane derivative by reaction of dimethylphenylphosphane with 1-azido-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose[7] in dry dichloromethane. Subsequent addition of the appropriate carbonyl compound affords the corresponding ligand, which can be purified by column chromatography. Complexes of type **I** (Table 1) with dimethyl fumarate (dmf), maleic anhydride (ma) or fumarodinitrile (Fig. 2) were prepared in good yield by starting from $[Pd(dba)_2]$ (dba = dibenzylideneacetone) according to a well established procedure,[4a] eqn. (1). After removal of the

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

solvent under vacuum, the complexes were obtained as yellow to orange microcrystalline solids by column chromatography. Alternatively, fdn or ma complexes could be prepared through olefin exchange by starting from the corresponding dmf complexes. Unfortunately, could we not isolate complexes of type **I** with ligand **5** (see Experimental). It is worth mentioning that the corresponding platinum complex [Pt(**5**)(fdn)] could be isolated in high yield.[8]

All the isolated complexes could be handled in air at room temperature and were stored for several weeks at 253 K without appreciable decomposition. fdn derivatives were found unaltered after several days in chloroform or dichloromethane solution, while [Pd(**3**)(ma)] and dmf complexes of both **3** and **4** slowly decomposed into palladium, olefin and "free" ligand. As discussed elsewhere,[4a,9] the stability of [Pd(N,N-chelate)(olefin)] complexes depends on the extent of π-back donation to the metal–alkene bond. Since fdn and ma are both better electron acceptors than dmf,[9c,10] it is reasonable that their complexes display higher stability.

NMR spectroscopy

The NMR properties of type **I** complexes can be summarized as follows. (i) The most prominent feature of the spectra is the large high-field shift of the olefin resonances, which is diagnostic of the above mentioned π-back donation contribution to the metal-alkene bond.[4a,9] Since the shift increases according to the electron-withdrawing ability of the olefin, fdn and ma signals undergo a larger shift.[11]

(ii) In the presence of prochiral olefins, such as fdn or dmf, complexes of type **I** may exist as diastereomers. Such diastereomeric pairs are claimed[4a,9c,d] to interconvert by olefin dissociation and subsequent re-co-ordination to the metal center with the opposite enantioface. When the process is slow on the NMR timescale[12] the signals pertaining to the diastereomers resonate separately. Alternatively average resonances are observed. NMR spectra (Table 1) of [Pd(**3**)(fdn)], [Pd(**4**)(fdn)], [Pd(**3**)(dmf)] and [Pd(**3**)(fdn)] in 0.015 M deuteriochloroform solution disclosed that the olefin exchange is slow at 298 K. Addition of free olefin (10–30%) caused broadening of the signals due to an increased exchange rate. Larger amounts of alkene averaged the signals giving rise to an unique sharp spectral pattern. These findings are consistent with the generally accepted associative mechanism for olefin exchange in complexes of type **I**.[4a,9c,d] Accordingly, broadening of the signals is expected to occur also by simply increasing the complex concentration, and this was proved in the case of [Pd(**3**)(fdn)].

Attempts to obtain the spectra at 328 K resulted in partial decomposition with formation of palladium, N,N-ligand and olefin. Only [Pd(**4**)(fdn)] remained unaltered at this temperature for several minutes, giving rise to an averaged spectrum.

Comparison of the just mentioned results with those obtained[4a] by using ligands of type **1** or **2** discloses that [Pd(N,N-chelate)(olefin)] complexes with the newly synthesized nitrogen chelates are less inert and stable. Actually, the spectra of the complexes containing the former ligands were little affected by increasing the temperature, and fast olefin exchange could be observed only in the presence of free olefin.

(iii) Type **I** complexes are typically involved in another dynamic process, *i.e.* alkene rotation around the metal–olefin bond. Information on its rate is available only when the olefin exchange is slow. On the grounds of their rotational symmetry the two halves of both dmf and fdn are expected to appear equivalent in the NMR spectra in the presence of fast rotation. The experimental evidence indicates that the alkene rotates

Table 1 Selected ^{1}H[a] and ^{13}C[b] NMR data for complexes of type **I**

	^{1}H			^{13}C			
	CH=N	6-R-py	olefin	C1[c]	C2–C5[c]	C6[c]	olefin
[Pd(**3**)(fdn)] isomer, 80%	8.71	8.89 (1 H, d)	2.9 (2 H, bd)	91.1	74.5 (1 C, b) 72.9 (2 C, b) 68.2 (1 C, b)	61.8	20.0 (2 C, b)
isomer, 20%	8.68	8.92 (1 H, d)	3.0 (2 H, b)	92.9	[d]	[d]	[d]
[Pd(**3**)(dmf)][e] isomer, 70%	8.65	8.81 (1 H, d)	3.95 (2 H, ABq)	93.3	74.4 (1 C) 73.5 (1 C) 72.1 (1 C) 68.2 (1 C)	62.2	43.0 (1 C) 42.3 (1 C)
isomer, 30%	8.71	8.78 (1 H, d)	3.92 (2 H, nm)	92.8	73.1 (1 C)[f]	63.0	[g]
[Pd(**4**)(fdn)] isomer, 80%	8.67	2.88 (3 H)	2.93 (2 H, ABq)	91.1	74.4 (1 C) 72.8 (1 C) 72.7 (1 C) 68.0 (1 C)	61.7	19.4 (1 C) 18.7 (1 C)
isomer, 20%	8.63	2.91 (3 H)	[g]	93.3	74.6 (1 C) 68.3 (1 C)[f]	62.3	19.4 (2 C)
[Pd(**4**)(dmf)] isomer, 70%	8.64	2.78 (3 H)	3.92 (2 H, ABq)	91.1	74.3 (1 C) 73.1 (1 C) 72.5 (1 C) 68.2 (1 C)	61.8	43.2 (1 C) 41.7 (1 C)
isomer, 30%	8.68	2.80 (3 H)	3.88 (2 H, nm)	91.1	74.7 (1 C) 73.6 (1 C) 68.6 (1 C)[f]	62.2	43.0 (1 C) 42.2 (1 C)
[Pd(**3**)(ma)][h,i]	8.68	8.83 (1 H, d)	4.00 (2 H, b)		72.5 (1 C) 72.1 (1 C) 71.3 (1 C) 68.0 (1 C)	62.3	41.0 (2 C, b)
[Pd(**4**)(ma)][h,j]	8.63	2.81 (3 H)	4.00 (2 H, b)	90.9	74.4 (1 C) 72.9 (1 C) 72.8 (1 C) 68.2 (1 C)	61.9	41.9 (1 C) 41.5 (1 C)
[Pd(**3***)(fdn)][k] isomer, 55%	8.67	2.88 (3 H)	2.93 (2 H, ABq)	97.2	80.4 (1 C) 78.6 (1 C) 74.3 (1 C) 71.7 (1 C)	63.7	[l]
isomer, 45%	8.63	2.91 (3 H)	[g]	98.2	80.7 (1 C) 78.9 (1 C) 75.7 (1 C) 72.3 (1 C)	63.7	[l]

[a] Recorded at 298 K and 250 MHz in $CDCl_3$ ($CHCl_3$, δ 7.26, as internal standard). Abbreviations: no attribute, singlet; b, broad signal; bd, broad doublet; d, doublet; nm, narrow multiplet; ABq, AB quartet. [b] Recorded at 298 K and 62.9 MHz in $CDCl_3$ ($^{13}CDCl_3$, δ 77, as internal standard). [c] Of glucoside. [d] Resonances averaged with those of the major isomer. [e] ^{13}C NMR spectrum recorded in CD_2Cl_2 ($^{13}CD_2Cl_2$, δ 53.8, as internal standard). [f] Other resonance/s hidden by those of the major isomer. [g] Hidden by other signals. [h] Mean resonances pertaining to both isomers. [i] ^{13}C NMR spectrum recorded in DMSO-d_6 ($(^{13}CD_3)_2SO$, δ 39.5, as internal standard). [j] Only the C1 signals are separate. That of the minor isomer resonates at δ 93.4. [k] In CD_3OD (CD_2HOD, δ 3.31, and $^{13}CD_3OD$, δ 49.3, as internal standards). [l] The olefin carbon atoms resonate at δ 19.6, 18.7, 17.6, 16.9. Owing to similar diastereomeric abundance the signals cannot unequivocally be attributed.

slowly at 298 K in both diastereomers of [Pd(**4**)(dmf)]. The same holds true at least for the most abundant isomer of the other fdn and dmf complexes. As for the minor ones, no clear conclusion could be reached since the pertaining resonances were often hidden by more intense signals.

(iv) According to the orientation of the olefin substituents, maleic anhydride derivatives of compounds **3** and **4** may exist as diastereomeric pairs. Beside olefin exchange, also rotation of the alkene can cause their interconversion. This occurs rapidly at room temperature as indicated by the presence of broad average resonances in the NMR spectra.

Table 2 Diastereomeric ratios of type **I** complexes at 298 K with ligands **3** and **4**

	Ratio	
Compound	In $CDCl_3$	In CD_2Cl_2
[Pd(**3**)(fdn)]	80:20	65:35
[Pd(**3**)(dmf)]	70:30	80:20
[Pd(**4**)(fdn)]	80:20	90:10
[Pd(**4**)(dmf)]	70:30	75:25
[Pd(**3***)(fdn)]	55:45[a]	

[a] In CD_3OD.

Enantioselectivity of olefin co-ordination

As mentioned above, type **I** complexes of fdn and dmf exist as two diastereomers. According to the NMR features the isomeric equilibrium is reached rapidly after dissolution of the complexes. Integration of suitable separated CH=N peaks allowed us to calculate the composition.

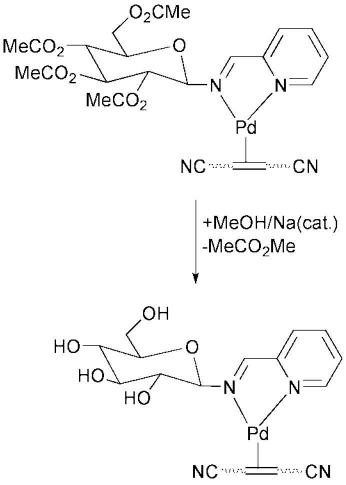
An inspection of Table 2 discloses that our expectation concerning an enhanced stereochemical activity of the new ligands was correct. In fact, both **3** and **4** discriminate one enantioface of fdn or dmf more effectively than the closely related ligands of type **1**. Actually, the diastereomeric ratios prompted by the former chelates are within the ranges 90:10–65:35 and 80:20–70:30, respectively in CD_2Cl_2 and $CDCl_3$. The values did not exceed 55:45[13] in $CDCl_3$ when type **1** ligands were co-ordinated.

This favorable trend could be inferred also in the case of the symmetrical ligand **5**. The NMR spectrum[14] of crude [Pd(**5**)(fdn)] (see Experimental) disclosed the presence of an unique diastereomer. We recall that the diastereomeric ratios prompted by the related type **2** ligands were within 97:3 and 75:25.[4a]

Synthesis of the water soluble complex [Pd(3*)(fdn)]

Water soluble palladium(0) compounds are rare.[15] As far as we know, none contains either a Pd–C bond or a chiral ligand, while both features are present in the previously[4a] described [Pd(**1M***)(fdn)]. During this work a new related complex was prepared with the aim of investigating the still unexplored potential of these species in catalysis (see next paragraph).

Basic hydrolysis of the acetyl groups in [Pd(**3**)(fdn)] (Scheme 2) afforded the corresponding hydrophilic [Pd(**3***)(fdn)] (**3*** indicates the deprotected form of **3**). The yellow microcrystalline product was isolated in high yield by addition of diethyl ether to the reaction mixture. The complex, which is fairly soluble in water and methanol, was characterized through NMR spectroscopy and elemental analyses. The two expected diastereomers (in 55 : 45 ratio) could separately be observed in CD_3OD solution at 298 K, while in D_2O the faster olefin exchange gave rise to an averaged spectrum. In the former solvent the presence of four separate signals for the olefin carbon atoms indicates that also olefin rotation is hindered at room temperature.



Scheme 2

Hydrogenation reactions

Increasing attention is currently addressed towards homogeneous metal catalysed synthesis in aqueous systems.[2a,h,i,6] However, it should be noted that it is difficult in whatsoever solvent to ascertain whether the reaction proceeds under heterogeneous or homogeneous conditions.[16] It is often found that both mechanisms operate. As an example, Elsevier and coworkers showed that [Pd(N,N-chelate)(dmf)] species (N,N chelate = *N*,*N′*-diaryldiiminoacenaphthene) promote the hydrogenation of alkenes[17a] or alkynes[17b] in dry tetrahydrofuran. They found[17a] that the reaction was homogeneous when electron-poor alkenes were employed, while olefins with donor substituents were mainly hydrogenated by metal particles which formed in the reacting system.

The availability of the hydrophilic complexes [Pd(**1M***)(fdn)] and [Pd(**3***)(fdn)], both fairly similar to the mentioned palladium(0) species used by Elsevier, offered the opportunity of investigating their ability in hydrogenating alkenes in water. Acrylonitrile, methacrylonitrile and crotononitrile (*cis*/*trans* mixture) were chosen as substrates on the following grounds: (i) the nitrile group can stabilize the corresponding olefin palladium(0) complexes by effective electron attraction; (ii) both the olefins and the corresponding hydrogenated products are not water soluble and can easily be extracted from the aqueous phase; (iii) the nitrile substituent is more resistant than other common organic functions (esters or amide) to hydrolysis; (iv) a comparison on the behavior of strictly related olefins displaying different structures or degrees of substitution is fairly easy.

In a typical experiment 0.010 mmol of catalyst was dissolved in 1 mL of water. The flask was evacuated and 0.50 mmol of the appropriate olefin was added. Hydrogen at atmospheric pressure was then admitted. After stirring at room temperature for the required time (see below), the organic compounds were extracted with 1 mL of deuteriochloroform containing 0.10 mmol of hexamethyldisiloxane (HMDS), and the mixture analysed through NMR spectroscopy. The presence of a known amount of HMDS us allowed to calculate yields by integration. By using [Pd(**1M***)(fdn)] as catalyst, hydrogenation was complete within two hours and the saturated products were extracted in high yield (>80–90%). Some decomposition was however observed, and the residue, tested according to the procedure described by Maitlis and co-workers,[16,18] was found to be very active. This result indicates that most of the reaction occurred under heterogeneous conditions.

As it is known that catalysed hydrogenation of olefins in water can be influenced by pH,[6b] the reactions were run in aqueous KOH at various concentrations with the same olefin : catalyst ratio as above. Sugars can epimerize in water in the presence of base, so the stability of [Pd(**1M***)(fdn)] under these conditions was preliminarily assessed. The complex was found unaltered after several hours in D_2O at pH 14.

After two hours in 1.0 M KOH, acrylonitrile, methacrylonitrile and crotononitrile were hydrogenated in 70, 50 and 50% yields, respectively. The metal containing residues recovered by filtration of the reaction mixture were almost inactive under the circumstances described by Maitlis and co-workers,[16] which indicates that hydrogenation is essentially homogeneous under strongly basic conditions. Reasonably, the suppression of the heterogeneous contribution determines the observed lower conversions with respect to those found in water.

When the reaction times were prolonged in order to increase the yield of products the amount of organic compounds extracted by chloroform decreased substantially (<30–40%), while that found in the water phase was negligible. It must be inferred that undesired concomitant processes occur, which, however, were not investigated.

For this reason the reactions were run at lower pH values, *i.e.* in 0.10 and 0.25 M KOH solutions. In 0.10 M KOH acrylonitrile was hydrogenated within two hours, while methacrylonitrile and crotononitrile required three hours to react completely. In all cases, the organic products were extracted in good to high yields (70–90%). Analysis of the activity of the residues disclosed that the homogeneous contribution to the reactions was substantial. After two hours the yields of saturated products were in the range 60–90%, while the amount of unchanged olefins was within 0–10%. On the other hand, when the residues were tested as catalysts under the same conditions as adopted in the initial runs, the yields were found to be 35–50 and 25–40%, respectively.

In 0.25 M KOH hydrogenation of acrylonitrile was again complete within two hours in high yield. The residue was found almost inactive, *i.e.* conversion of acrylonitrile into propionitrile was less than 5% after the same time.[20] Instead, the clear filtered solution was able to hydrogenate freshly added acrylonitrile with small loss of activity. These results indicate that the reaction is essentially homogeneous under these conditions.

Methacrylonitrile and crotonitrile were also hydrogenated in 0.25 M KOH. After two hours saturated products and unchanged olefins were recovered in 50–60 and 5–25% yield, respectively. These ranges became 15–30 and 50–60%, respectively, in the reactions promoted by the corresponding residues.

It should be noted that in none of the experiments hydrolysis of the nitrile was found to occur. This could easily be checked by recording the ^{13}C NMR spectra of the products. Actually, signals at δ 120 were diagnostic of the presence of CN groups,

Table 3 Elemental analyses (%) for the new compounds

Compound	Formula	C found (calc.)	H found (calc.)	N found (calc.)
3	$C_{20}H_{24}N_2O_9$	54.83 (55.04)	5.69 (5.54)	6.50 (6.42)
4	$C_{21}H_{26}N_2O_9$	56.25 (56.00)	5.81 (5.82)	6.36 (6.22)
5	$C_{30}H_{40}N_2O_{18}$	50.03 (50.28)	5.52 (5.63)	3.79 (3.91)
[Pd(**3**)(fdn)]	$C_{24}H_{26}N_4O_9Pd$	46.59 (46.43)	4.34 (4.22)	8.78 (9.02)
[Pd(**3**)(dmf)]	$C_{26}H_{32}N_2O_{13}Pd$	45.27 (45.46)	4.56 (4.70)	4.05 (4.08)
[Pd(**4**)(fdn)]	$C_{25}H_{28}N_4O_9Pd$	47.30 (47.29)	4.54 (4.44)	8.94 (8.82)
[Pd(**4**)(dmf)]	$C_{27}H_{34}N_2O_{13}Pd$	46.07 (46.26)	4.75 (4.89)	4.01 (4.00)
[Pd(**3**)(ma)]	$C_{24}H_{26}N_2O_{12}Pd$	45.16 (44.98)	4.20 (4.09)	4.41 (4.37)
[Pd(**4**)(ma)]	$C_{25}H_{28}N_2O_{12}Pd$	46.02 (45.85)	4.42 (4.31)	4.27 (4.28)
[Pd(**3***)(fdn)]	$C_{16}H_{18}N_4O_5Pd$	42.27 (42.45)	3.93 (4.01)	12.65 (12.37)

while no resonances were found in the typical range of carbonyl frequencies.

Complex [Pd(**3***)(fdn)] was also tested in the hydrogenation of the alkene-1-nitriles. On the grounds of the mentioned findings the reactions were performed in 0.10 and 0.25 M KOH. A close analogy with the results obtained by using [Pd(**1M***)(fdn)] was found, the only difference consisting in a slightly improved activity in 0.25 M KOH. Once the experimental conditions which allowed the catalysis to be mostly homogeneous were found an enantioselective reduction of the double bond was attempted. The substrate α-ethylacrylonitrile[21] was hydrogenated in 0.25 M KOH by either [Pd(**3***)(fdn)] or [Pd(**1M***)(fdn)]. In both cases the product of the reaction, 2-methylbutyronitrile, did not show significant optical rotatory power.[22] The same held true when the reaction was performed in dry THF by using [Pd(**4**)(dmf)] as catalyst. The unsuccessful outcome of these experiments is in keeping with the lack of literature reports on asymmetric hydrogenations of alkenes catalysed by palladium complexes. Actually, as far as we know, this catalysis has been achieved only under heterogeneous conditions,[23] while no examples of homogeneous hydrogenation have so far been reported.

Conclusion

This paper describes new chiral nitrogen chelates based on carbohydrates and the corresponding palladium(0) complexes of formula [Pd(N,N-chelate)(olefin)]. The nitrogen donor is directly linked to the chiral C1 atom of a glucose moiety. This feature enhances the ability of the ligands to induce enantioselective co-ordination of prochiral olefins with respect to that displayed by related chelates where the N-donor is bonded to the sugar *via* the methylene C6 atom.

A new water soluble palladium(0) complex was also prepared. This compound and a previously reported related species were examined as catalysts in the hydrogenation of unsaturated nitriles in water. It was found that the pH of the solvent plays a crucial role in determining both yield and reaction course. More precisely, in distilled water hydrogenation is fast, but essentially heterogeneous. In 1.0 M KOH hydrogenation is homogeneous, but parallel undesired reactions lower the yield of the products. Best conditions for the homogeneous hydrogenation of acrylonitrile were found in 0.25 M KOH, where the yield of propionitrile was high. Under these conditions the reaction involving methacrylonitrile and crotononitrile also proceeds readily, but a heterogeneous contribution is present. This latter finding can be rationalized by considering that the stability of [Pd(N,N-chelate)(olefin)] complexes grows when the steric hindrance and/or the donor properties of the alkene decrease. Thus, with substituted alkenenitriles formation of metal particles may occur faster than in the presence of acrylonitrile.

Experimental

NMR spectra were recorded with a 250 MHz spectrometer (Bruker Model AC-250). The solvent was $CDCl_3$ ($CHCl_3$, δ 7.26, and $^{13}CDCl_3$, δ 77, as internal standards). The following abbreviations are used for describing NMR multiplicities: no attribute, singlet; d, doublet; dd, double doublet; m, multiplet; t, triplet. Specific optical rotatory powers [*α*] were measured with a Perkin-Elmer Polarimeter (Model 141) at 298 K and 589 nm in dichloromethane ($c = 1.0$ g per 100 mL). 1-Azido-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose[7] was prepared according to a literature method. Dichloromethane was distilled from calcium hydride, methanol from magnesium immediately before use. Elemental analyses for the new compounds are reported in Table 3.

Syntheses

Compounds 3, 4 and 5. To a stirred solution of $PPhMe_2$ (0.14 g, 1.0 mmol) in 5 mL of dry dichloromethane kept in an ice-bath a solution of 1-azido-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose (0.37 g, 1.0 mmol) in 5 mL of dry dichloromethane was added dropwise. After the addition was complete, the ice-bath was removed and formation of nitrogen was observed. The progress of the reaction was monitored by TLC analysis on silica with ethyl acetate–light petroleum (bp 40–60 °C) (1 : 1) as eluent. The reaction affording the corresponding iminophosphorane was complete within 30 minutes. To the solution was added the appropriate carbonyl compound in stoichiometric amount (respectively 1.0 mmol of 6-methyl-2-pyridinecarbaldehyde or 2-pyridinecarbaldehyde, and 0.50 mmol of glyoxal as a 40% w/w water solution). When glyoxal was employed sodium sulfate was also added. After 15 minutes of stirring the volume was reduced under vacuum and the mixture filtered on Florisil (15 × 1.5 cm) with ethyl acetate–light petroleum (1 : 1) as eluent. Removal of the solvents under vacuum afforded the microcrystalline products in 70–80% yield. ^1H NMR: **3**, δ 8.61 (1 H, d), 8.51 (1 H), 7.98 (1 H, d), 7.33 (1 H, dd), 7.32 (1 H, t), 5.37 (1 H, t), 5.14 (1 H, t), 4.99 (1 H, t), 4.93 (1 H, dd), 4.28 (1 H, dd), 4.18 (1 H, dd), 3.89 (1 H, m), 2.07 (3 H), 2.02 (3 H), 2.01 (3 H) and 1.99 (3 H); **4**, 8.50 (1 H), 7.80 (1 H, d), 7.61 (1 H, t), 7.18 (1 H, d), 5.36 (1 H, t), 5.14 (1 H, t), 4.99 (1 H, t), 4.88 (1 H, dd), 4.28 (1 H, dd), 4.18 (1 H, dd), 3.89 (1 H, m), 2.57 (3 H), 2.07 (3 H), 2.02 (6 H) and 2.01 (3 H); **5**, 8.00 (2 H, d), 5.31 (2 H, t), 5.11 (2 H, t), 4.90 (2 H, t), 4.84 (2 H, dd), 4.25 (2 H, dd), 4.16 (2 H, dd), 3.83 (2 H, m), 2.06 (6 H), 2.04 (6 H), 2.01 (6 H) and 2.00 (6 H). Selected ^{13}C resonances (at 62.9 MHz): **3**, δ 162.5 (CH=N), 149.4 (C6 of pyridine), 136.6, 125.4, 121.5 (C3–C5 of pyridine), 92.3 (C1 of glucose), 73.7, 73.3, 71.8, 68.3 (C2–C5 of glucose) and 62.1 (C6 of glucose); **4**, 162.7 (CH=N), 136.9, 125.1, 118.6 (C3–C5 of pyridine), 92.3 (C1 of glucose), 73.7, 73.4, 71.9, 68.4 (C2–C5 of glucose), 62.1 (C6 of glucose) and 24.2 (6-Me of pyridine); **5**, 161.2 (CH=N), 91.7 (C1 of glucoses), 73.7, 73.3, 71.3, 68.1 (C2–C5 of glucoses) and 61.9 (C6 of glucoses); [*α*]: **3**, −16; **4**, −45; **5**, −19 deg $cm^3\ g^{-1}\ dm^{-1}$.

[Pd(N,N-chelate)(olefin)] complexes I. 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 the solvent was removed under vacuum. The residue was separated by chromatography on silica gel with dichloromethane (to remove dba) and then with dichloromethane–methanol (40 : 1). The solvents were removed under vacuum from the collected yellow-orange fractions affording the product as a yellow-orange 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(**3**)(dmf)] (0.69 g, 0.10 mmol) in 1 mL of dichloromethane was added fdn (0.012 g, 0.15 mmol). The resulting solution was chromatographed as described above affording pure [Pd(**3**)(fdn)] (yield 80–85%). Attempts to prepare [Pd(**5**)(fdn)] according to eqn. (1) led to copious formation of a black precipitate. The deuteriochloroform extract was found to contain mainly **5**, dba and fdn, while only 10–20% of the material consisted of the desired complex. The mother-liquor was found to contain dba in substantial amounts. Attempts to purify the crude product were unsuccessful. Better results were not obtained either by changing the solvent of the reaction, or by using other alkenes, *i.e.* acrylonitrile and dimethyl fumarate.

[Pd(3*)(fdn)]. To a stirred suspension of [Pd(**3**)(fdn)] (0.012 g, 0.20 mmol) in 2.5 mL of dry methanol was added a catalytic amount of sodium methoxide in the same solvent. After 30 minutes formation of a yellow solution ensued, and the product was crystallized by addition of diethyl ether. The complex was separated, washed with diethyl ether (3 × 3 mL) and dried under vacuum (yield: 90%).

Hydrogenation reactions

In a typical experiment 0.010 mmol of either [Pd(**1M***)(fdn)] or [Pd(**3***)(fdn)] was dissolved in 1 mL of water (or appropriate KOH solution) in a 50 mL flask with a rubber stopper and an outlet connected to a vacuum line. The flask was evacuated and 0.50 mmol of the appropriate olefin was added with a syringe through the rubber stopper. The vacuum line was replaced by an hydrogen reservoir at atmospheric pressure and the gas introduced into the flask. After stirring at room temperature the organic compounds were extracted with 1 mL of deuteriochloroform containing 0.10 mmol of hexamethyldisiloxane, and the mixture analysed through NMR spectroscopy.

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