Easy Synthesis of New Chiral Tridentate Schiff Bases and Their Use as [N,N,O] Ligands for Ni and Pd Complexes − Catalytic Behaviour versus Hydrogenation Reactions[‡]

Camino González-Arellano,[a,b] Enrique Gutiérrez-Puebla,[a] Marta Iglesias,*[a] and Félix Sánchez*[b]

Keywords: Palladium / Nickel / Chiral Schiff bases / Hydrogenation / Tridentate ligands

The chiral [N,N,O] tridentate unsymmetrical Schiff bases **3**–**5** (aryl = phenyl, 1-naphthyl, 2-naphthyl) were synthesised easily in high purity and good yields. All the organic compounds were characterised by elemental analysis, mass spectrometry, IR, ^{1}H and ^{13}C NMR spectroscopy. Palladium(II) and nickel(II) Schiff-base complexes were prepared as air-stable solids. Because the [N,N,O] ligand is tridentate after deprotonation of the –OH group, the coordination of the metal ion is completely stereospecific and gives rise to only one diastereoisomer. The X-ray crystal structures of the complexes [Ni(**3**)(OAc)] and [Pd(**4**)(OAc)] were determined. These complexes were shown to be very active catalysts (TOF up to 10^6 h^{-1}) for the hydrogenation of olefins and imines under mild conditions.

Introduction

The development of efficient catalytic asymmetric reactions is one of the most challenging tasks in current synthetic chemistry, much effort having been devoted to the creation of new chiral N-ligands and their metal complexes for evaluation in advanced asymmetric catalysis.[1] The condensation of an amine and an aldehyde, to form Schiff bases, was one of the earliest reported reactions in chemistry;[2] these compounds are now an important class of ligands in coordination chemistry, and have been studied extensively[3] because of their selectivity for various metal ions. Jacobsen and Katsuki have developed tetradentate salen ligands, now one of the most intensely studied classes of bis-chiral Schiff bases, able to coordinate easily to a wide variety of metals. The interest in such bases has increased since the discovery of manganese(III) salen complexes, which are excellent catalysts for the enantiomeric epoxidation of unfunctionalized alkenes;[4] the development of chiral salen metal complexes and catalysts in the last decade has therefore shown a very rapid growth.[5] Chiral salen-containing complexes are now used as catalysts for a variety of enantioselective reactions such as oxidation, aziridination, cyclopropanation, Diels−Alder cyclisation, and hydrogenation.[6]

In this report, we focus on new simpler chiral Schiff-base ligands containing pyrrolidinylamino functionalities (in place of one of the phenolic groups on salen ligands), the synthesis of the complexes [Pd(**L**)(OAc)] (**LPd**), [Ni(**L**)(OAc)] (**LNi**), as well as the X-ray crystal structures of **3Ni** and **4Pd**. The method we have developed should allow the easy synthesis of a wide variety of chiral Schiff-base ligands. The iminophenoxy ligands were designed to coordinate to Pd^{II} and Ni^{II}; the amino substituent could be varied in order to improve the stability of the complexes in the catalytic hydrogenation of alkenes and imines.

Results and Discussion

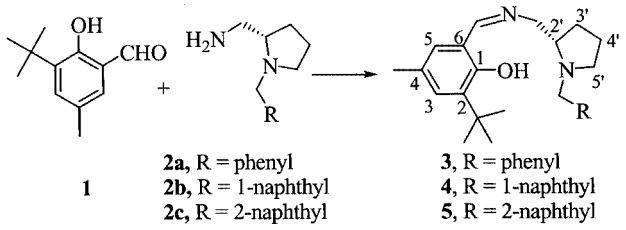
Synthesis of Ligands

The synthesis of chiral ligands **3**−**5** is based on the condensation of enantiomerically pure (*S*)-(1-benzylpyrrolidin-2-yl)methylamine (**2a**), (*S*)-[1-(1-naphthylmethyl)pyrrolidin-2-yl]methylamine (**2b**) and (*S*)-[1-(2-naphthylmethyl)pyrrolidin-2-yl]methylamine (**2c**) with 3-*tert*-butyl-2-hydroxy-5-methylbenzaldehyde (**1**) in the presence of 3 Å molecular sieves (Scheme 1). The chiral amines **2b** and **2c** were synthesized from (*S*)-proline in a simple sequence of reactions (Scheme 2), with the chiral centre remaining unmodified. The preparation of the benzyl analogue **2a** was efficiently

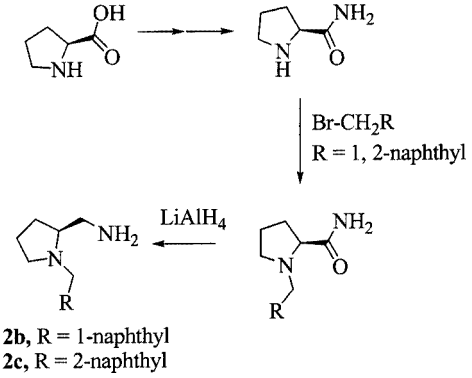
[‡] Preliminary results were presented in the 6th International Symposium on Catalysis Applied to Fine Chemicals (Delft, 2003).

[a] Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain
Fax: (internat.) +34-913720623
E-mail: marta.iglesias@icmm.csic.es
[b] Instituto de Química Orgánica General, CSIC, Juan de la Cierva, 3, 28006 Madrid, Spain,
Fax: (internat.) +34-915644853
E-mail: felix-iqo@iqog.csic.es

carried out by the procedure published by us previously.[7] Compounds **3−5** were characterised by elemental analysis (C, H, N), ^{1}H and ^{13}C NMR and mass spectrometry. In the ^{1}H NMR spectra, the OH protons appear at δ = 9.80 ppm (for **4**) and the imine protons appear as singlets at δ = 8.18 (for **3**), 8.00 (for **4**) and 8.30 (for **5**) ppm. NOE experiments indicate unequivocally that the ligands prefer the *anti* configuration.



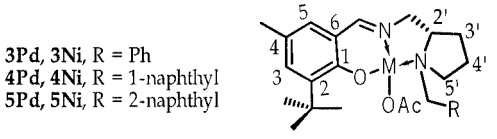
Scheme 1. General synthesis of chiral Schiff bases **3−5**



Scheme 2. Synthesis of chiral amine precursors

Synthesis of the Complexes

The interest in making new salen-type ligands lies in their ability to form stable complexes with transition metals, thus serving as potential precursors for homogeneous catalysis of a variety of reactions.[5,8] We decided to use a chiral catalyst employing a chiral ligand in which the stereogenic centres are in close proximity to the metal (Scheme 3); chiral predetermination was observed for all of the palladium and nickel complexes.[9] When the chiral ligands are coordinated to the metal, two chiral centres are introduced, at the coordinated nitrogen atom and at the metal. From the ORTEP diagrams and the NMR spectroscopic data, we can deduce that the coordination of the metal ion is completely stereospecific, and gives rise to only one of the two possible diastereoisomers.



Scheme 3. General structural formulae of complexes **3Pd, 3Ni**, **4Pd**, **4Ni**, **5Pd** and **5Ni**

All the complexes were prepared by addition of the divalent metal salts [$Pd(OAc)_2$, $Ni(OAc)_2$] to an ethanolic solution of ligand; one of the acetate groups is displaced by the phenolic anion whereas the amine and imine nitrogen atoms coordinate to the metal in a square planar arrangement (Scheme 3). The complexes, which were precipitated from EtOH, were obtained with high purity and in high yields as microcrystalline stable solids, which are soluble in organic solvents. The structures of all the complexes were confirmed by elemental analysis (C, H, N and M), IR spectroscopy, and ^{1}H and ^{13}C NMR spectroscopy. They were also characterised by electro-spray mass spectrometry. The ES-MS spectra of complexes show the molecular ion peaks, [M^+], and peaks from the fragments due to elimination of the acetate ion [$M^+ - OAc$]. All assignments were confirmed by good agreement between the observed and calculated isotopic distributions.

Infrared and Electronic Spectra

IR stretching frequencies were used to characterize the binding of the imine nitrogen. Bands at 1600 cm^{-1} were assigned to the $\nu_{C=C}$ and $\nu_{C=N}$ vibrations, shifted to lower wavenumbers (relative to the free ligands) due to N-coordination of the imine.[10] The absence of the ν_{O-H} band (present in the spectra of the free ligands at ca. 3430 cm^{-1}) is in accordance with loss of the hydroxyl proton. The IR spectra also show strong bands at 1290 and ca. 1500 cm^{-1}; these were assigned to the symmetric and asymmetric ν_{COO} bands, respectively, in agreement with the values expected for monocoordinate acetate ligands.[11] New bands in the 500−600 cm^{-1} region were ascribed to ν_{M-O}.

The electronic absorption spectra for all complexes in the 200−800 nm range were obtained using 10^{-3} to 10^{-5} M solutions in ethanol. The complexes show several band maxima in the UV region, assigned to the intraligand π→π* and n→π* transitions in the aromatic ring and the azomethine group and the charge-transfer transitions.[12] The higher molar extinction coefficient of the bands in the 260−350 nm range may be due to the coincidence of the charge transfer, d→π* and intraligand π→π* and n→π* transitions. The bands in the 400−450 nm region correspond to the d→d transitions expected for planar complexes[13] and MLCT bands.

NMR Spectra

The diamagnetic palladium and nickel complexes were characterised by ^{1}H and ^{13}C NMR spectroscopy. All assignments were based on several correlations in the 2D spectra, and are fully consistent with the structures depicted in Scheme 3. In all cases, the spectra show the simultaneous occurrence of two sets of signals, which are attributable to the substituted benzaldimine entity and the aliphatic part of the ligand. In the ^{1}H NMR spectra all the resonances were high-field shifted compared to the uncoordinated ligand, and they were in agreement with metallation of the ligand and coordination of the metal atom to the imine nitrogen atom. The most noticeable shifts observed were

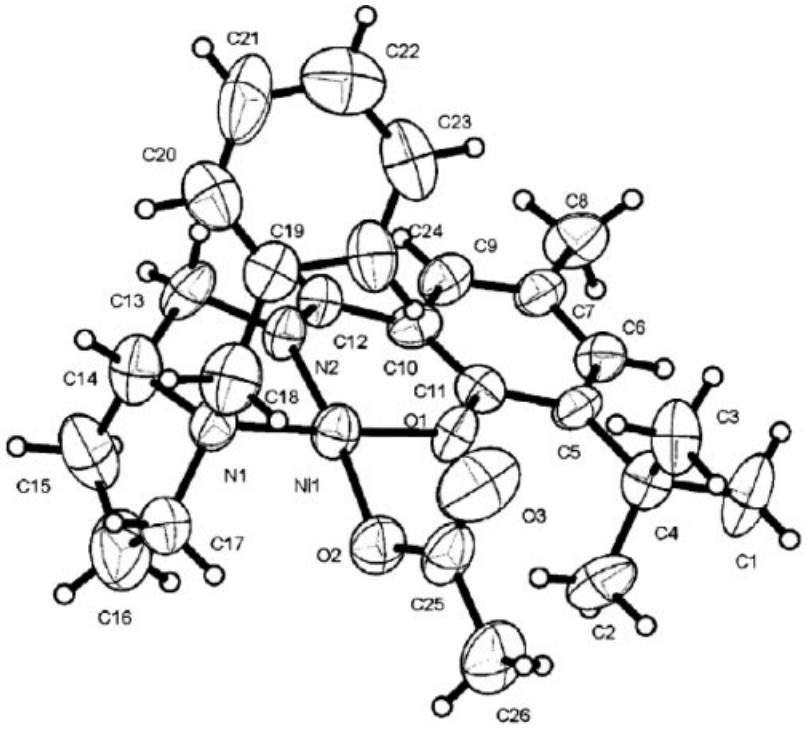


Figure 1. Molecular structure of **3Ni**, with labelling scheme; only one molecule has been shown for clarity

those for C*H*=N, CH=NCH_2, H-2′ and H-5′. Deprotonation of the hydroxyl group was confirmed by the absence of OH resonances in the ^{1}H NMR spectrum. The resonance corresponding to the C*H*=N proton appears as a singlet (δ = 7.9−7.2 ppm), shifted to high field due to the coordination of the imine group to the metal atom through the lone pair of the nitrogen atom.[14] The ^{1}H NMR spectrum shows the *Me*COO protons as a singlet at δ = 2.10 ppm. The ^{13}C NMR spectra show that the signals assigned to the *C*=N carbons are shifted to high-field and those due to C-1 shifted downfield (to δ ≈ 162 ppm), confirming that metallation had occurred.

Crystal Structure Studies of 3Ni and 4Pd

Suitable crystals were grown by slowly evaporating an ethanolic solution of the complex. The molecular structures are shown in Figure 1 and Figure 2. Crystal data are given in Table 4, and selected bond lengths and angles with estimated standard deviations are shown in Table 1.

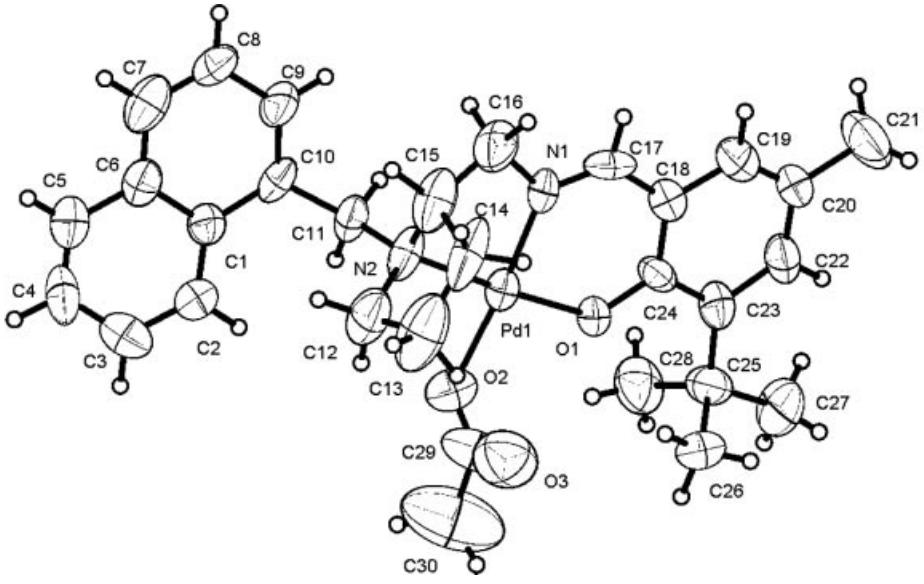


Figure 2. Molecular structure of **4Pd**, with labelling scheme

Table 1. Selected bond lengths (Å) and angles (°) for complexes **3Ni** and **4Pd**

3Ni		**4Pd**	
Ni(1)−O(1)	1.825(5)	Pd(1)−O(1)	1.975(5)
Ni(1)−N(1)	1.947(6)	Pd(1)−N(2)	2.072(6)
Ni(1)−O(2)	1.851(6)	Pd(1)−O(2)	2.054(8)
Ni(1)−N(2)	1.834(7)	Pd(1)−N(1)	1.925(8)
Ni(2)−O(4)	1.863(6)		
Ni(2)−N(4)	1.941(6)		
Ni(2)−O(5)	1.863(6)		
Ni(2)−N(3)	1.841(7)		
O(1)−Ni(1)−N(2)	93.3(3)	N(1)−Pd(1)−O(1)	94.1(3)
O(1)−Ni(1)−O(2)	87.4(2)	O(1)−Pd(1)−O(2)	89.2(3)
N(2)−Ni(1)−O(2)	170.7(3)	N(1)−Pd(1)−O(1)	175.3(3)
O(1)−Ni(1)−N(1)	176.1(3)	O(1)−Pd(1)−N(2)	175.4(3)
N(2)−Ni(1)−N(1)	87.7(3)	N(1)−Pd(1)−N(2)	83.0(3)
O(2)−Ni(1)−N(1)	92.3(3)	O(2)−Pd(1)−N(2)	93.5(3)
O(3)−Ni(2)−N(3)	94.5(3)		
O(3)−Ni(2)−O(4)	86.7(2)		
N(3)−Ni(2)−O(4)	169.3(3)		
O(3)−Ni(2)−N(4)	176.0(3)		
N(3)−Ni(2)−N(4)	88.0(3)		
O(4)−Ni(2)−N(4)	91.5(3)		

The structure consists of ML(OAc) molecules; each asymmetric unit of **3Ni** contains two crystallographically independent molecules (only one molecule is shown). The absolute configuration is assigned on the basis of known chirality of the amine used. The ligands are tridentate, and bond to the M^{II} atom by the deprotonated phenolic oxygen atom (O_{phe}) and the imine (N_{im}) and tertiary amine nitrogens (N_{am}); each metal also coordinates to one acetate group. The geometry of metal coordination sphere is distorted square planar, and the sum of the angles around the metal atom is 360.7(4)° for the Ni complex and 359.8(4)° for the Pd complex. The angles between adjacent atoms in the coordination sphere are close to the expected value of 90°, with the most noticeable distortions found for the N−M−N angle, due to chelation [N(2)−Ni(1)−N(1): 87.7(3)°, N(3)−Ni(2)−N(4): 88.0(3)°, N(1)−Pd−N(2): 83.0(3)°]. The $M-O_{phe}$, $M-N_{im}$ and $M-N_{am}$ distances were found to be 1.825, 1.863; 1.834, 1.841 and 1.947, 1.941 [Ni(1), Ni(2)] for **3Ni** and 1.975, 1.925 and 2.072 for **4Pd** in good agreement with the literature values.[15] Furthermore, the pyrrolidine metal distances [$M-N_{am}$: 1.947(6) for the free ligand, 1.941(6) for **3Ni** and 2.072(6) Å for **4Pd**] are longer than the $M-N_{im}$ distances, despite the fact that amine nitrogen atoms usually show stronger coordination than imine nitrogen atoms. This effect, however, is probably caused by greater steric hindrance of the tertiary amine nitrogen compared to the mono-substituted imine nitrogen. The coordinated atoms lie exactly in plane (the maximum deviation from least-squares plane is 0.002 Å) and are arranged at the corners of an irregular quadrilateral, reflecting the difficulty that the ligand has in spanning the square-planar coordination positions. The structures contain one six-membered and one five-membered chelate ring. The six-membered metallacycle containing the imino moiety is practically coplanar with the O(1)−O(2) coordination plane [dihedral angles 8.21(0.27)° for Ni(1), 10.07(0.27)° for Ni(2) in **3Ni**, 7.13(0.46)° for **4Pd**]. The five-membered metallacycle is in an envelope conformation, on C(15) for **4Pd**, and on C(14) [Ni(1)] and C(40′) [Ni(2)] for **3Ni**. The pyrrolidine rings are also in an envelope conformation. In **3Ni**, the 1-benzylpyrrolidine group of the ligand **3** is in close proximity to the nickel ion.

Catalytic Hydrogenation

These structurally well-defined Ni^{II} and Pd^{II} complexes enable us to explore their application to catalytic hydrogenation. The hydrogenation of the simple alkenes **I** and **II**, the functionalized alkenes **III**−**V** and the imines **VI** and **VII** (Figure 3) with Pd and Ni complexes were carried out under standard conditions (EtOH, 4 atm. H_2, 40 °C). The results are summarised in Table 2 and Table 3.

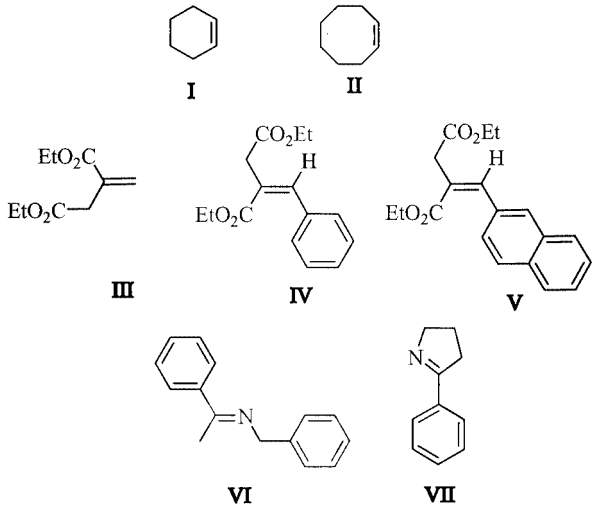


Figure 3. Substrates used in the hydrogenation reactions

Table 2. Turnover rates for catalytic hydrogenation with ligand **3** (TOF: h^{-1}; Conditions: 4 atm, 40 °C, S/C ratio 1000:1)

Substrate	Pd	Ni
I	5460	4020
II[a]	25500	22800
III	3360	2400
IV	640	220
V	153	117
VI	3240	4800
VII	167	93

[a] S/C ratio 10000:1.

The nature of the metal center has an influence on the catalytic activity. In general, the palladium catalysts were more active than their nickel analogues when **3** was used as ligand under our conditions; the nickel complexes were the most active when **4** or **5** were used. The complexes **4Pd**, **4Ni**, **5Pd** and **5Ni** contain naphthyl groups as substituents in the pyrrolidinyl group, and display TOFs of 8×10^5 to 10^6 h^{-1} for the hydrogenation of cyclooctene (**II**) and 3−5

Table 3. Turnover rates for catalytic hydrogenation with ligands **4** and **5** (TOF: h^{-1}; Conditions: 4 atm, 40 °C S/C ratio 100000:1).

Catalyst	II	VI
4Pd	842760	337500
4Ni	964320	410940
5Pd	684000	309240
5Ni	961920	461520

$\times 10^5$ h^{-1} for imine **VI**. This may be due to the closeness of the phenyl group to the metal (Figures 1 and 2). Use of these Pd and Ni complexes led to quantitative conversion of the olefins under the hydrogenation conditions employed. No palladium black or nickel was formed in any of the hydrogenation reactions. Low enantiomeric excesses (< 10% *ee*) resulted in all cases, as shown by ^{1}H NMR spectroscopy and chiral GCMS of the reaction mixtures.

The accumulated evidence concerning the mechanisms of homogeneously catalysed hydrogenations indicates that there are three principal modes of hydrogen activation: oxidative addition, and homolytic or heterolytic hydrogen cleavage. In the case of the Pd and Ni complexes, heterolytic cleavage is preferred to a hydride intermediate, which would have to involve charge separation without any oxidation of the metal.[16]

Conclusion

A series of chiral [N,N,O] tridentate Schiff bases were synthesised with high purity and in good yield. Treatment of these ligands with palladium(II) and nickel(II) acetate in EtOH gave only one diastereoisomer of the respective air-stable complexes. These complexes were shown to be active catalysts for hydrogenation, with high reactivity under mild conditions (TOF up to 10^6 h^{-1}). These simple catalysts, especially the cheaper Ni complexes, are a real alternative to conventional Pd catalysts for hydrogenation in industrial processes.

Experimental Section

General Remarks: All preparations of metal complexes were carried out under nitrogen by conventional Schlenk techniques. Solvents were carefully degassed before use. C, H, N analyses were carried out by the analytical department of the Institute of Materials Science (C.S.I.C.) with a perkin-Elmer 240C apparatus. Metal contents were analysed by atomic absorption using Perkin−Elmer Analyst 300 atomic absorption and Plasma ICP Perkin−Elmer 40 spectrometers. IR spectra were recorded with a Nicolet XR60 spectrophotometer (range 4000−200 cm^{-1}) in KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were taken on Varian XR300 and Bruker 200 spectrometers. Chemical shifts are referred to tetramethylsilane (internal standard). Optical rotation values were measured using the sodium-D line (589 nm) with a Perkin−Elmer 241 MC polarimeter. Gas chromatography analysis was performed using a Hewlett−Packard 5890 II apparatus with a flame ionisation detector in a cross-linked methylsilicone column.

2-*tert*-Butyl-4-methyl-6-[(*E*)-({[(2*S*)-1-benzylpyrrolidin-2-yl]methyl}-imino)methyl]phenol (3): A solution of (*S*)-(1-benzylpyrrolidin-2-yl)methylamine (**2a**) (380 mg, 2 mmol) in ethanol (20 mL) was added to a solution of 3-*tert*-butyl-5-methylsalicylaldehyde (384 mg, 2 mmol) in ethanol (20 mL) at room temperature over a period of 30 min with stirring. The solvent was removed under vacuum, and the residue purified by flash chromatography (hexane:EtOAc, 5:1) to give a yellow oil (640 mg). Yield 88%. $[\alpha]_D^{25} = -14.3$ (c = 0.5, EtOH). $C_{24}H_{32}N_2O$ (364): calcd. C 79.1, H 8.8, N 7.7; found C 78.9, H 8.6, N 7.4. IR (film, cm^{-1}): $\tilde{\nu}$ = 1628, 1592 (C=C + C=N). UV/Vis (λ, nm): 221, 262, 332. ^{1}H NMR ($CDCl_3$, ppm): δ = 8.18 (s, C*H*=N), 7.10−7.20 (m, 5 H_{arom}, H_{Bzl}), 7.05−7.00 (m, H_{arom}), 6.82−6.77 (m, H_{arom}), 3.95, 3.35 (d, J_{AB} = 13.4 Hz, CH_2Ph), 3.69−3.61 (m, CH=NCH_2), 3.45−3.35 (m, CH=NCH_2), 2.94−2.85 (m, $H^{5'a}$); 2.83−2.73 (m, $H^{2'}$), 2.24−2.12 (m, CH_3, $H^{5'b}$), 1.98−1.87 (m, $H_{3'a}$), 1.71−1.54 (m, $H^{3'b}$, $H^{4'a,b}$), 1.35 [s, C(CH_3)$_3$] ppm. ^{13}C NMR ($CDCl_3$): δ = 166.23 (*C*H=N), 158.35 (C_1), 139.75 (C_{arom}), 137.17 (C^6), 130.27 (C^5), 129.40 (C_2), 128.78 (C_{arom}), 128.17 (C_{arom}), 126.81 (C_{arom}), 126.30 (C^3), 118.47 (C^4), 64.20 ($C^{2'}$), 63.87 (CH=NCH_2), 59.32 (CH_2Ph), 54.67 ($C^{5'}$), 34.70 [*C*(CH$_3$)$_3$], 29.59 ($C^{3'}$), 29.40 [C(*C*H$_3$)$_3$], 22.84 ($C^{4'}$), 20.61 (CH_3). MS (EI) (*m*/*z*, %): 364 (1) [M^+]; 160 (M^+ − 184, 100); 91 (M^+ − 69, 47).

[(2*S*)-1-(1-Naphthylmethyl)pyrrolidin-2-yl]methylamine (2b): K_2CO_3 (1.38 g, 10 mmol) and 1-bromomethylnaphthalene[17] (2.21 mg, 10 mmol) were added to a solution of pyrrolidin-2-carboxamide[18] (114 mg, 1 mmol) in acetonitrile (30 mL). The mixture was stirred for 24 h and purified by flash chromatography (eluant: hexane), to provide (2*S*)-1-(1-naphthylmethyl)pyrrolidine-2-carboxamide. Yield 70%. M.p. 159−161 °C. $[\alpha]_D^{25} = -5.1$ (c = 0.9, $CHCl_3$). $C_{16}H_{18}N_2O$ (254): calcd. C 75.6, H 7.1, N 11.0; found C 75.3, H 7.3, N 10.9. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3393 (NH), 1650 (C=O). ^{1}H NMR ($CDCl_3$, ppm): δ = 8.10−8.00 (m, H_{arom}), 7.80−7.60 (m, 2 H_{arom}), 7.50−7.20 (m, 4 H_{arom}), 6.80−6.70 (m, NH_2), 4.87−4.68 (m, NH_2), 4.20−3.98 (m, $CH_2^{naphthyl}$), 3.21−2.97 (m, $H^{2'}$, $H^{5'a}$), 2.54−2.37 (m, $H^{5'b}$), 2.30−2.10 (m, $H^{3'a}$), 1.95−1.63 (m, $H^{3'b}$, $H^{4'a}$), 1.22−1.10 (m, $H^{4'b}$). ^{13}C NMR ($CDCl_3$): δ = 179.91 (*C*=O), 136.21 (C_{arom}), 135.71 (C_{arom}), 133.94 (C_{arom}), 130.81 (C_{arom}), 130.24 (C_{arom}), 128.98 (C_{arom}), 128.12 (C_{arom}), 127.60 (C_{arom}), 127.35 (C_{arom}), 125.28 (C_{arom}), 69.57 ($C^{2'}$), 60.07 ($CH_2^{naphthyl}$), 57.04 ($C^{5'}$), 32.81 ($C^{3'}$), 26.24 ($C^{4'}$). MS (EI) (*m*/*z*, %): 210 (56), 141 (100).

$LiAlH_4$ (3.8 g, 100 mmol) was added to a solution of (2*S*)-1-(1-naphthylmethyl)pyrrolidine-2-carboxamide (2.54 g, 10 mmol) in THF (15 mL), and the mixture stirred at reflux for 12 h. After workup, **2b** was obtained as a yellow oil. Yield 97%. $[\alpha]_D^{25} = -29.6$ (c = 0.9, $CHCl_3$). $C_{16}H_{20}N_2$ (240): calcd. C 80.0, H 8.3, N 11.7; found C 80.1, H, 8.6, N 11.5. IR (film, cm^{-1}): $\tilde{\nu}$ = 3368 (NH). ^{1}H NMR ($CDCl_3$, ppm): δ = 8.30−8.20 (m, H_{arom}), 7.95−7.67 (m, 2 H_{arom}), 7.60−7.28 (m, 4 H_{arom}), 4.41, 3.72 (2 H, J_{AB} = 13 Hz, $CH_2^{naphthyl}$), 2.95−2.87 (m, $H^{5'a}$), 2.80−2.74 (m, CH_2NH_2), 2.73−2.61 (m, $H^{2'}$), 2.37−2.20 (m, $H^{5'b}$), 2.04−1.89 (m, $H^{3'a}$), 1.78−1.62 (m, $H^{3'b}$, $H^{4'a,b}$) ppm. ^{13}C NMR ($CDCl_3$): δ = 128.45 (C_{arom}), 127.70 (C_{arom}), 126.69 (C_{arom}), 125.76 (C_{arom}), 125.65 (C_{arom}), 125.52 (C_{arom}), 125.48 (C_{arom}), 125.20 (C_{arom}), 124.15 (C_{arom}), 124.05 (C_{arom}), 66.12 ($C^{2'}$); 57.48 ($CH_2^{naphthyl}$), 55.05 ($C^{5'}$), 44.33 (CH_2NH_2), 28.10 ($C^{3'}$), 23.24 ($C^{4'}$). MS (EI) (*m*/*z*, %): 212 (90); 141 (100).

2-*tert*-Butyl-4-methyl-6-[(*E*)-({[(2*S*)-1-(1-naphthylmethyl)pyrrolidin-2-yl]methyl}imino)methyl]phenol (4): The method and conditions described for the synthesis of **3** were used. Reaction of 3-*tert*-butyl-5-methylsalicylaldehyde (384 mg, 2 mmol) with [(2*S*)-1-(1-naph-

thylmethyl)pyrrolidin-2-yl]methylamine (**2b**) (480 mg, 2 mmol), and flash chromatography (hexane/ethyl acetate) gave **4** as a yellow oil in 52% yield. $[\alpha]_D^{25} = -17.6$ (c = 0.9, $CHCl_3$). $C_{28}H_{34}N_2O$ (414): calcd. C 81.1, H 8.3, N 6.7; found C 79.9, H 8.4, N 6.5. IR (film, cm^{-1}): $\tilde{\nu}$ = 1628, 1592 (C=C + C=N). UV/Vis (λ, nm): 240, 266, 349. ^{1}H NMR ($CDCl_3$, ppm): δ = 9.80 (s, O*H*), 8.22−8.18 (m, $H_{arom,}$), 8.00 (s, CH=N), 7.78−7.66 (m, 2 H_{arom}), 7.43−7.29 (m, H_{arom}), 7.03−7.01 (m, H_{arom}), 6.74−6.71 (m, H_{arom}) 4.33, 3.82 (d, J_{AB} = 13 Hz, $CH_2^{naphthyl}$), 3.70−3.61 (m, CH=NC*H*$_2$), 3.36−3.32 (m, CH=NC*H*$_2$), 2.93−2.80 (m, H$^{2',5'a}$), 2.33−2.16 (m, C*H*$_3$, H$^{5'b}$), 2.05−1.90 (m, H$^{3'a}$), 1.78−1.57 (m, H$^{3'b}$, H$^{4'a,b}$), 1.36 [s, C(CH$_3$)$_3$] ppm. ^{13}C NMR ($CDCl_3$): δ = 165.33 (*C*H=N); 157.32 (C$^{1\ arom}$), 136.09 (C_{arom}), 134.75 (C_{arom}), 134.39 (C_{arom}), 132.73 (C_{arom}), 130.43 (C_{arom}), 129.43 (C_{arom}), 128.46 (C_{arom}), 127.35 (C_{arom}), 126.77 (C_{arom}), 125.72 (C_{arom}), 124.78 (C_{arom}), 124.57 (C_{arom}), 124.24 (C_{arom}), 123.60 (C_{arom}), 117.42 (C_{arom}), 63.95 (C$^{2'}$), 62.72 (CH=N*C*H$_2$), 56.93 ($CH_2^{naphthyl}$), 54.14 (C$^{5'}$), 33.70 [*C*(CH$_3$)$_3$], 28.68 (C$^{3'}$), 28.38 [C(*C*H$_3$)$_3$], 22.02 (C$^{4'}$), 19.65 (CH$_3$). MS (EI) (*m*/*z*, %): 414 (2) [M$^+$]; 210 (25); 141 (100).

[(2*S*)-1-(2-Naphthylmethyl)pyrrolidin-2-yl]methylamine (2c): K_2CO_3 (1.38 g, 10 mmol) and 2-bromomethylnaphthalene (2.21 mg, 10 mmol) were added to a solution of pyrrolidin-2-carboxamide (114 mg, 1 mmol) in acetonitrile (30 mL). The mixture was stirred for 24 h and purified by flash chromatography (hexane/ethyl acetate), to provide (2*S*)-1-(2-naphthylmethyl)pyrrolidin-2-carboxamide as a white solid. Yield 72%. M.p. 140−143 °C. $[\alpha]_D^{25} = -35.0$ (c = 1, $CHCl_3$). $C_{16}H_{18}N_2O$ (254): calcd. C 75.6, H 7.1, N 11.0; found C 75.2, H 7.0, N 11.2. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3401 (NH); 1632 (C=O). ^{1}H NMR ($CDCl_3$, ppm): δ = 7.85−7.63 (m, 4 H_{arom}), 7.51−7.22 (m, 3 H_{arom}), 6.02−5.90 (m, NH_2), 4.11, 3.62 (d, J_{AB} = 13 Hz, $CH_2^{naphthyl}$), 3.28−2.23 (m, H$^{2'}$), 3.07−3.01 (m, H$^{5'a}$), 2.44−2.34 (m, H$^{5'b}$), 2.31−2.20 (m, H$^{3'a}$), 2.05−1.97 (m, H$^{3'b}$), 1.84−1.72 (m, H$^{4'a,b}$) ppm. ^{13}C NMR ($CDCl_3$): δ = 178.08 (C=O); 136.04 (C_{arom}); 133.28 (C_{arom}), 132.66 (C_{arom}), 128.14 (C_{arom}), 127.66 (C_{arom}), 127.62 (C_{arom}), 127.15 (C_{arom}), 126.77 (C_{arom}), 126.13 (C_{arom}), 125.77 (C_{arom}), 67.44 (C$^{2'}$), 59.95 ($CH_2^{naphthyl}$), 53.87 (C$^{5'}$), 30.60 (C$^{3'}$), 24.03 (C$^{4'}$). MS (EI) (*m*/*z*, %): 210 (48); 141 (100).

$LiAlH_4$ (3.8 g, 100 mmol) was added to a solution of (2*S*)-1-(2-naphthylmethyl)pyrrolidin-2-carboxamide (2.54 g, 10 mmol) in THF (15 mL) and the mixture stirred at reflux temperature for 12 h. After workup, **2c** was obtained as a yellow oil (2.54 g, 10 mmol). Yield 91%. $[\alpha]_D^{25} = -39.9$ (c = 0.8, $CHCl_3$). $C_{16}H_{20}N_2$ (240): calcd. C 80.0; H; 8.3; N; 11.6; found C 79.8; H 8.4; N 11.5. IR (film, cm^{-1}): $\tilde{\nu}$ = 3361 (NH). ^{1}H NMR ($CDCl_3$, ppm): δ = 7.93−7.70 (m, 4 H_{arom}), 7.54−7.40 (m, 3 H_{arom}), 4.17, 3.48 (d, J_{AB} = 14.4 Hz, $CH_2^{naphthyl}$), 3.04−2.90 (m, H$^{5'a}$), 2.83−2.74 (m, C*H*$_2$NH$_2$), 2.65−2.56 (m, H$^{2'}$), 2.32−2.20 (m, H$^{5'b}$), 2.20−1.87 (m, H$^{3'a}$), 1.82−1.62 (m, H$^{3'b}$, H$^{4'a,b}$) ppm. ^{13}C NMR ($CDCl_3$): δ = 137.48 (C_{arom}), 133.32 (C_{arom}), 132.60 (C_{arom}), 127.81 (C_{arom}), 127.62 (C_{arom}), 127.60 (C_{arom}), 127.18 (C_{arom}), 126.91 (C_{arom}), 125.86 (C_{arom}), 125.43 (C_{arom}), 65.60 (C$^{2'}$), 59.28 ($CH_2^{naphthyl}$), 54.67 (C$^{5'}$), 44.12 (*C*H$_2$NH$_2$), 27.96 (C$^{3'}$), 22.96 (C$^{4'}$). MS (EI) (*m*/*z*, %): 212 (96); 141 (100).

2-*tert*-Butyl-4-methyl-6-[(*E*)-({[(2*S*)-1-(2-naphthylmethyl)pyrrolidin-2-yl]methyl}imino)methyl]phenol (5): The method and conditions described for the synthesis of **4** were used. Reaction of 3-*tert*-butyl-2-hydroxy-5-methylbenzaldehyde (384 mg, 2 mmol) with [(2*S*)-1-(2-naphthylmethyl)pyrrolidin-2-yl]methylamine (**2c**) (480 mg, 2 mmol), and flash chromatography (hexane/ethyl acetate) gave **5** as a yellow oil in 58% yield. $[\alpha]_D^{25} = -37.4$ (c = 0.9, $CHCl_3$). $C_{28}H_{34}N_2O$ (414): calcd. C 81.1, H 8.3, N 6.8; found C 81.1, H 8.3, N 6.4. IR (film, cm^{-1}): $\tilde{\nu}$ = 1628, 1594 (C=C + C=N). UV/Vis (λ, nm): 240, 266, 334. ^{1}H NMR ($CDCl_3$, ppm): δ = 8.30−8.19 (m, C*H*=N), 7.86−7.71 (m, 4 H_{arom}), 7.51−7.40 (m, 3 H_{arom}), 7.12−7.09 (m, H^3); 6.86−6.81 (m, H^5); 4.18, 3.58 (d, J_{AB} = 19 Hz, $CH_2^{naphthyl}$), 3.82−3.40 (m, CH=NC*H*$_2$), 3.10−2.80 (m, H$^{2'}$, H$^{5'a}$), 2.36−2.24 (m, C*H*$_3$, H$^{5'b}$), 2.10−1.88 (m, H$^{3'a}$), 1.82−166 (m, H$^{3'b}$, H$^{4'a,b}$), 1.41 [s, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR ($CDCl_3$): δ = 166.75 (CH=N), 158.74 (C^1), 137.88 (C_{arom}), 137.54 (C_{arom}), 133.83 (C_{arom}), 133.12 (C_{arom}), 130.72 (C_{arom}), 129.88 (C_{arom}), 128.23 (C_{arom}), 128.16 (C_{arom}), 128.03 (C_{arom}), 127.71 (C_{arom}), 127.46 (C_{arom}), 126.76 (C_{arom}), 126.27 (C_{arom}), 125.88 (C_{arom}), 118.85 (C_{arom}), 64.82 (C$^{2'}$), 64.38 (CH=N*C*H$_2$), 60.02 ($CH_2^{naphthyl}$), 55.33 (C$^{5'}$), 35.16 [*C*(CH$_3$)$_3$], 30.04 (C$^{3'}$), 29.83 [C(*C*H$_3$)$_3$], 23.36 (C$^{4'}$), 21.08 (CH$_3$). MS (EI) (*m*/*z*, %): 414 (2) [M$^+$]; 210 (100); 141 (95).

Preparation of Metal Complexes. General Method: An solution of $Pd(OAc)_2$ or $Ni(OAc)_2$ in ethanol (0.5 mmol/15 mL) was added to a solution of the ligand in EtOH (15 mL) at room temperature. The resulting mixture was stirred under reflux for 4 hours, cooled to room temperature and then concentrated under vacuum. The residue was washed several times with diethyl ether, dried and filtered to afford the complex in almost quantitative yield.

[Pd(3)(OAc)] (3Pd): M.p. 218−220 °C. $[\alpha]_D^{25} = -34.8$ (c = 1, EtOH). $C_{26}H_{34}N_2O_3Pd$ (528): calcd. C 59.0, H 6.4, N 5.3, Pd 20.1; found C 58.6, H 6.6, N 5.1, Pd 19.8. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1614−1600 (C=C + C=N), 557 (Pd−O). UV/Vis (λ, nm) = 235, 259, 289, 420. ^{1}H NMR ($CDCl_3$, ppm): δ = 7.79−7.72 (m, 2 H_{arom}), 7.41−7.32 (m, 3 H_{arom}), 7.23 (s, CH=N), 7.11−7.07 (m, H_{arom}), 6.74 (s, H_{arom}), 4.82, 4.13 (d, J_{AB} = 9 Hz, CH_2Ph), 3.57−3.48 (m, CH=NC*H*$_2$, H$^{5'a}$), 3.29−3.20 (m, CH=NC*H*$_2$), 3.10−3.00 (m, H$^{4'a}$), 2.78−2.65 (m, H$^{2'}$), 2.50−2.40 (m, H$^{5'b}$), 2.17 (s, CH$_3$), 2.10−2.03 (m, OOCC*H*$_3$), 1.98−1.87 (m, H$^{3'a,b}$), 1.86−1.75 (m, H$^{4'b}$), 1.26 [s, C(C*H*$_3$)$_3$]. ^{13}C NMR ($CDCl_3$): δ = 178.26 (−OO*C*CH$_3$), 162.88 (*C*−O−Pd), 159.84 (*C*H=N), 140.66, 133.68, 131.99, 131.89, 130.65, 129.10, 128.74, 122.64, 119.94 (C_{arom}), 65.41 (*C*$^{2'}$), 63.12 (CH=N*C*H$_2$), 61.77 (CH_2Ph), 58.71 (C$^{5'}$), 35.36 [*C*(CH$_3$)$_3$], 29.37 [C(*C*H$_3$)$_3$], 27.48 (C$^{3'}$), 23.72 (CH$_3$), 22.57 (C$^{4'}$), 20.33 (OOC*C*H$_3$). MS$^+$ (EI) (*m*/*z*, %): 469 (M$^+$ − Ac, for ^{106}Pd), 471 (M$^+$ − Ac, for ^{108}Pd), 473(M$^+$ − Ac, for ^{110}Pd), 467 (M$^+$ − Ac, for ^{104}Pd), 465 (M$^+$ − Ac, for ^{102}Pd).

[Ni(3)(OAc)] (3Ni): M.p. 153−156 °C. $[\alpha]_D^{25} = -2.8$ (c = 1, EtOH). $C_{26}H_{34}N_2O_3Ni$ (481): calcd. C 64.8, H 7.0, N 6.0, Ni 12.3; found C 64.6, H 7.4, N 5.9, Ni 11.9. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1612−1590 (C=C + C=N), 554 (Ni−O). UV/Vis (λ, nm): 230, 264, 345, 425. ^{1}H NMR ($CDCl_3$, ppm): δ = 8.21 (s, 2 H_{arom}), 7.75 (s, H_{arom}), 7.42−7.35 (m, 2H_{arom}, CH=N), 6.93 (s, H_{arom}), 6.56 (s, H_{arom}), 4.90, 3.83 (d, J_{AB} = 10.5 Hz, CH_2Ph), 3.78−3.70 (m, H$^{5'a}$), 3.45 (s, H$^{4'a}$), 3.25−3.12 (m, CH=NC*H*$_2$), 2.98−2.83 (m, CH=NC*H*$_2$), 2.37−2.27 (m, H$^{2'}$), 2.18−2.07 (m, C*H*$_3$, OCOCC*H*$_3$, H$^{4'b}$, H$^{3'a}$), 1.95−1.83 (m, H$^{5'b}$, H$^{3'b}$), 1.23 [s, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR ($CDCl_3$): δ = 178.33 (OO*C*CH$_3$); 162.13 (*C*−O−Ni); 161.69 (*C*H=N), 141.12, 132.34, 132.23, 131.97, 128.95, 128.77, 128.67, 122.74, 119.67 (C_{arom}), 62.22 (C$^{2'}$), 61.36 (CH=N*C*H$_2$), 59.29 (*C*H$_2$Ph), 56.65 (C$^{5'}$), 34.88 [*C*(CH$_3$)$_3$], 29.13 [C(*C*H$_3$)$_3$], 27.85 (C$^{3'}$), 24.53 (CH$_3$), 22.91 (C$^{4'}$), 20.36 (OOC*C*H$_3$). MS$^+$ (EI) (*m*/*z*, %): 422 (M$^+$, ^{59}Ni); 423 (M$^+$, ^{60}Ni).

[Pd(4)(OAc)] (4Pd): Yield 65%. M.p. 211−215 °C. $[\alpha]_D^{25} = -4.3$ (c = 0.5, $CHCl_3$). $C_{30}H_{36}N_2O_3Pd$ (578): calcd. C 62.3, H 5.9, N 4.8, Pd 18.3; found C 62.0, H 6.2, N 5.1, Pd 17.7. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1616−1598 (C=C + C=N), 514 (Pd−O). UV/Vis (λ, nm): 243, 288, 423. ^{1}H NMR ($CDCl_3$, ppm): δ = 8.27−8.10 (m, H_{arom}), 7.90−7.77 (m, H_{arom}, CH=N), 7.60−7.38 (m, H_{arom}), 7.12−7.02

(m, H_{arom}), 6.72−6.66 (m, H_{arom}), 5.20, 4.95 (d, J_{AB} = 16 Hz, $CH_2^{naphthyl}$), 3.77−3.37 (m, $H^{5'a}$, CH=NCH_2), 3.22−2.76 (m, $H^{2'}$, CH=NCH_2), 2.17−2.05 (m, $H^{5'b}$, CH_3, OCOCH_3), 1.93−1.47 (m, $H^{3'a,b}$, $H^{4'a,b}$), 1.34−1.21 [s, C(CH_3)$_3$] ppm. ^{13}C NMR ($CDCl_3$): δ = 178.80 (O*C*OCH$_3$), 163.33 (*C*−O−Pd), 160.33 (CH=N), 133.72, 131.93, 131.39, 131.06, 130.77, 130.53, 129.39, 129.30, 128.22, 127.51, 126.60 (C_{arom}), 125.51 123.97 123.11 120.40 (C_{arom}), 65.42 ($C^{2'}$), 63.29 (CH=NCH_2), 60.11 ($C^{5'}$), 58.75 ($CH_2^{naphthyl}$), 35.79 [*C*(CH$_3$)$_3$], 29.78 [C(*C*H$_3$)$_3$], 27.47 ($C^{3'}$), 24.14 ($C^{4'}$), 23.16 (CH_3), 20.76 (OCO*C*H$_3$). MS$^+$ (EI) (*m*/*z*, %): 519 (M^+ − Ac, for ^{106}Pd); 521 (M^+ − Ac, for ^{108}Pd); 523 (M^+ − Ac, for ^{110}Pd); 517 (M^+ − Ac, for ^{104}Pd); 515 (M^+ − Ac, for ^{102}Pd).

[Ni(4)(OAc)] (4Ni): Yield 75%. M.p. 218−222 °C. $[\alpha]_D^{25}$ = −1.9 (*c* = 0.9, $CHCl_3$). $C_{30}H_{36}N_2O_3Ni$ (531): calcd. C 67.8, H 6.8, N 5.4, Ni 11.1; found C 67.6, H 7.0, N 5.3, Ni 10.9. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1614−1600 (C=C + C=N), 518 (Ni−O). UV/Vis (λ, nm): 245, 267, 346, 428. ^{1}H NMR ($CDCl_3$, ppm): δ = 8.41−8.32 (m, 2 H_{arom}), 7.92−7.83 (m, 2 H_{arom}), 7.67−7.45 (m, 3 H_{arom}), 7.34 (s, CH=N), 6.97−6.91 (m, H_{arom}), 6.62−6.57 (m, H_{arom}), 5.15−5.02 (m, $CH_2^{naphthyl}$), 3.80−3.64 (m, $H^{4'a}$), 4.15−3.83 (m, $H^{5'a}$), 3.45−3.20 (m, $H^{5'b}$, CH=NCH_2), 3.01−2.82 (m, CH=NCH_2), 2.57−2.38 (m, $H^{2'}$), 2.23−2.12 (m, OCOCH$_3$, $H^{3'a}$), 2.05 (s, CH_3), 1.95−1.56 (m, $H^{3'b}$, $H^{4a,b}$), 1.40−1.12 [s, C(CH_3)$_3$] ppm. ^{13}C NMR ($CDCl_3$): δ = 178.75 (O*C*OCH$_3$), 162.61 (*C*−O−Ni), 162.20 (*C*H=N), 141.50, 134.18, 133.80, 132.70, 131.2, 130.40, 129.32, 129.09, 128.69, 127.38, 126.54, 125.57, 124.11, 123.15, 120.13 (C_{arom}), 62.37 ($C^{2'}$); 61.70 (CH=N*C*H$_2$), 57.06 ($CH_2^{naphthyl}$), 54.18 ($C^{5'}$), 35.32 [*C*(CH$_3$)$_3$], 30.09 [C(*C*H$_3$)$_3$], 29.60 ($C^{3'}$), 28.11 (CH_3), 24.85 ($C^{4'}$), 20.79 (OCO*C*H$_3$). MS$^+$ (EI) (*m*/*z*, %): 472 (M^+ − Ac, for ^{59}Ni), 473 (M^+ − Ac, for ^{60}Ni).

[Pd(5)(OAc)] (5Pd): Yield 65%. M.p. 208−211 °C. $[\alpha]_{435}^{25}$ = +1.9 (*c* = 0.9, $CHCl_3$). $C_{30}H_{36}N_2O_3Pd$ (578): calcd. C 62.3, H 5.9, N 4.8, Pd 18.3, found C 62.0, H 6.0, N 5.2, Pd 17.9. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1618−1599 (C=C + C=N), 514 (Pd−O). UV/Vis (λ, nm): 245, 290, 424. ^{1}H NMR ($CDCl_3$, ppm): δ = 8.10−8.03 (m, H_{arom}), 8.00−7.96 (m, CH=N), 7.85−7.75 (m, 4 H_{arom}), 7.50−7.38 (m, 2 H_{arom}), 7.18−7.16 (m, H_{arom}), 7.07−7.02 (m, H_{arom}), 4.95, 4.26 (d, J_{AB} = 13.8 Hz, $CH_2^{naphthyl}$), 3.60−3.37 (m, $H^{5'a}$, CHN=CH_2), 3.24−3.15 (m, CH=NCH_2), 2.83−2.71 (m, $H^{2'}$), 2.58−2.42 (m, $H^{5'b}$), 2.17−2.04 (m, OCOCH$_3$, CH_3), 1.97−1.83 (m, $H^{3'a,b}$, $H^{4'a,b}$), 1.40−1.25 [s, C(CH_3)$_3$] ppm. ^{13}C NMR ($CDCl_3$): δ = 176.23 (O*C*OCH$_3$), 160.92 (C−O−Pd), 157.81 (CH=N), 138.70, 131.63 130.95, 129.38, 128.62, 127.53, 127.19, 126.68, 126.50, 126.07, 125.75, 124.87, 124.60, 121.14, 117.91 (C_{arom}), 63.62 ($C^{2'}$), 61.23 (CH=N*C*H$_2$), 59.98 ($CH_2^{naphthyl}$), 56.85 ($C^{5'}$); 33.39 [*C*(CH$_3$)$_3$], 28.88 [C(*C*H$_3$)$_3$], 27.38 ($C^{3'}$), 25.50 (CH_3), 21.78 ($C^{4'}$), 18.34 (OCO*C*H$_3$). MS$^+$ (EI) (*m*/*z*, %): 519 (M^+ − Ac, for ^{106}Pd); 521 (M^+ − Ac, for ^{108}Pd); 523 (M^+ − Ac, for ^{110}Pd); 517 (M^+ − Ac, for ^{104}Pd); 515 (M^+ − Ac, for ^{102}Pd).

[Ni(5)(OAc)] (5Ni): Yield 73%. M.p. 223−226 °C. $[\alpha]_D^{25}$ = −0.7 (*c* = 0.9, $CHCl_3$). $C_{30}H_{36}N_2O_3Ni$ (531): calcd. C 67.8, H 6.8, N 5.3, Ni 11.1; found C 67.6, H 7.0, N 5.3, Ni 11.5. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1612−1600 (C=C + C=N), 540 (Ni−O). UV/Vis (λ, nm): 241, 267, 346, 428. ^{1}H NMR ($CDCl_3$, ppm): δ = 8.70−8.60 (m, H_{arom}), 8.30−8.27 (s, H_{arom}), 7.93−7.85 (s, CH=N), 7.85−7.75 (m, 3 H_{arom}), 7.50−7.38 (m, 2 H_{arom}), 6.92−6.85 (m, H^3), 6.55−6.48 (m, H^5), 5.00, 3.91 (d, J_{AB} = 16.3 Hz, $CH_2^{naphthyl}$), 3.80−3.64 (m, $H^{4'a}$), 3.45−3.35 (m, $H^{5'a}$), 3.18−3.07 (m, CH=NCH_2), 2.91−2.80 (m, CH=NCH_2), 2.38−2.27 (m, $H^{2'}$), 2.17−2.00 (m, OCOCH$_3$, $H^{3'a}$, $H^{5'b}$), 1.98−1.75 (m, CH_3, $H^{3'b}$, $H^{4'b}$), 1.00−0.96[s, C(CH_3)$_3$]

Table 4. Crystallographic data for complexes **3Ni** and **4Pd**

	3Ni	**4Pd**
Empirical formula	$C_{26}H_{34}N_2NiO_3$	$C_{30}H_{36}N_2O_3Pd$
Molecular mass	481.26	579.01
T [K]	296(2)	296(2)
λ [Å]	0.71073	0.71073
Crystal system	monoclinic	orthorhombic
Space group	*C*2	$P2_12_12_1$
a (Å)	36.337(4)	7.9823(12)
b (Å)	9.0865(9)	10.6063(16)
c (Å)	15.5821(16)	32.171(5)
β [°]	103.878(2)	
V (Å^3)	4994.7(9)	2723.7(7)
Z	8	4
D (calcd.) [g/cm^3]	1.280	1.412
μ [mm^{-1}]	0.805	0.714
F(000)	2048	1200
Crystal size [mm]	0.40 × 0.15 × 0.10	0.16 × 0.16 × 0.12
θ range [°]	3.65 to 31.10	3.84 to 26.40
Index ranges	$-49 \le h \le 52$, $-11 \le k \le 13$, $-21 \le l \le 20$	$-9 \le h \le 9$, $0 \le k \le 13$, $0 \le l \le 40$
Reflections collected	15515	5315
Independent reflections	9891 [R_{int} = 0.0867]	5315 [R_{int} = 0.0000]
Completeness to θ [%]	81.1	97.7
Absorption correction	Multi-scan (SADABS)	Multi-scan (SADABS)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	9891/1/588	5315/0/331
Goodness-of-fit on F^2	0.805	1.047
Final *R* indices [$I > 2\sigma(I)$]	$R1$ = 0.0653, $wR2$ = 0.1561	$R1$ = 0.0683, $wR2$ = 0.1156
R indices (all data)	$R1$ = 0.1665, $wR2$ = 0.1814	$R1$ = 0.1399, $wR2$ = 0.1295
Absolute structure parameter	0.02(6)	0.08(6)
Extinction coefficient	0.0000(2)	0.0044(7)
Largest diff. peak and hole [e·Å^3]	2.283 and −0.325	1.101 and −0.491

ppm. ^{13}C NMR ($CDCl_3$): δ = 163.50 (C−O−Ni), 163.25 (*C*H=N), 142.63, 134.77, 134.52, 133.67, 132.71, 131.70, 130.75, 130.10, 130.00, 129.52, 129.22, 128.21, 128.01, 124.17, 121.14 (C_{arom}), 64.10 ($C^{2'}$), 63.07 (CHN=*C*H_2), 61.23 ($CH_2^{naphthyl}$), 58.56 ($C^{5'}$), 32.32 [*C*$(CH_3)_3$], 30.63 [C(*C*$H_3)_3$], 29.39 ($C^{3'}$), 25.97 (CH_3), 24.45 ($C^{4'}$), 21.79 (OCO*C*H_3). MS^+ (EI) (*m*/*z*, %): 472 (M^+ − Ac, for ^{59}Ni); 473 (M^+ − Ac, for ^{60}Ni).

Catalytic Experiments: The catalytic properties of the Pd and Ni complexes with respect to hydrogenation were examined under conventional conditions for batch reactions in a 100 mL reactor (Autoclave Engineers) at 40 °C, using 4 atm. hydrogen pressure and a metal/substrate molar ratio of 1/1000. The progress of the reaction and the optical purity (*ee*) of the hydrogenated product were monitored by gas chromatography with a chiral glass capillary column {stationary phase: a mixture of methyl silicone (OV-1701) and methylsilicone heptakis[2,3-dipentyl-6-(*tert*-butyldimethylsilyl)]-β-cyclodextrin}.[19]

X-ray Crystallography: Three-dimensional, room temperature X-ray data were collected on a Bruker−Siemens Smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (molybdenum, λ = 0.71073 Å) operating at 50 kV and 20 mA. Data were collected over a quadrant of the reciprocal space by a combination of two frame sets. The cell parameters were determined and refined by least-squares fit of all the reflections collected. Each frame exposure time was 10 s covering 0.3° in ω. The crystal-to-detector distance was 6.05 cm. Coverage of the unique set was over 81.1% (**3Ni**), 97.7% (**4Pd**), complete to at least 31.10° (Ni), 26.40° (Pd) in θ. The first 50 frames were re-collected at the end of the data collection to monitor crystal decay; this showed a drop in the intensities to about 60% of their initial values. The Flack *x* parameters were 0.02(6) and 0.08(6), indicative of a correct absolute structure. The structure was solved by Multan and Fourier methods using SHELXTL.[20] Full matrix least-square refinement was carried out by using SHELXTL[20] minimising $w(F^2_o - F^2_c)^2$. The crystal of **3Ni** showed a very poor spectrum at high angles; thus, about 18% of the reflections gave negative intensities after the integration process. Because of this, only positive reflections (81.1%) were taken into account. Weighted *R* factors (*Rw*) and all goodness of fit parameters *S* are based on F^2, conventional *R* factors (*R*) are based on *F*. Crystal data are given in Table 4.

CCDC-218738 (for **4Pd**) and -218739 (for **3Ni**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

Financial support by the Dirección General de Investigación Científica y Técnica of Spain (Project MAT2000−1768-C02−02) is gratefully acknowledged.

[1] F. Fache, E. Schulz, M. L. Tommasino, M. Lemaire, *Chem. Rev.* **2000**, *100*, 2159−2231.
[2] H. Schiff, *Ann. Suppl.* **1864**, *3*, 343.
[3] G. Shing, P. A. Shing, A. K. Sen, K. Shing, S. N. Dubey, R. N. Handa, J. Choi, *Synth. React. Inorg. Met.-Org. Chem.* **2002**, *32*, 171−187.
[4] [4a] T. Katsuki, in *Catalytic Asymmetric Synthesis* (Ed.: I. Ojima), John Wiley & Sons, New York, **2000**, chapter 6, p. 287. [4b] E. N. Jacobsen, M. H. Wu, in *Comprehensive Asymmetric Catalysis II* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer Verlag, New York, **1999**, chapter 18, p. 649. [4c]K. Smith, C. Liu, *Chem. Commun.* **2002**, 886−887.
[5] [5a] L. Canali, D. C. Sherrington, *Chem. Soc. Rev.* **1999**, *28*, 85−93. [5b] D. A. Atwood, M. J. Harvey, *Chem. Rev.* **2001**, *101*, 37−52.
[6] [6a] Y. N. Ito, T. Katsuki, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 603−619. [6b] V. Ayala, A. Corma, M. Iglesias, F. Sánchez, *J. Catal.*, in press.
[7] [7a] M. J. Alcón, M. Iglesias, F. Sánchez, I. Viani, *J. Organomet. Chem.* **2000**, *601*, 284−292. [7b] M. T. Rispens, O. J. Gelling, A: H. De Vries, A. Meetsma, F. van Bolhuis, B. L. Feringa, *Tetrahedron* **1996**, *52*, 3521−3546.
[8] F. Lake, C. Moberg, *Eur. J. Org. Chem.* **2002**, 3179−3188 and references cited therein.
[9] U. Knof, A. von Zelewsky, *Angew. Chem. Int. Ed.* **1999**, *38*, 302−322 and references cited therein.
[10] [10a] H. Onoue, I. Moritani, *J. Organomet. Chem.* **1972**, *43*, 431−436. [10b] H. Onoue, K. Minami, K. Nakagawa, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3480−3485.
[11] K. Nakamoto, *IR and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley & Sons, New York, **1997**.
[12] T. N. Sorrell, W. E. Allen, P. S. White, *Inorg. Chem.* **1995**, *34*, 952.
[13] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, **1984**.
[14] Y. Ustynyuk, V. A. Chertkov, J. V. Barinov, *J. Organomet. Chem.* **1971**, *29*, C53.
[15] [15a] T. Koga, H. Furutachi, T. Nakamura, N. Fusita, M. Ohba, K. Takahashi, H. Okawa, *Inorg. Chem.* **1998**, *37*, 989−996. [15b] S. Uozumi, H. Furutachi, M. Ohba, H. Okawa, D. E. Fenton, K. Shindo, S. Murata, D. J. Kitko, *Inorg. Chem.* **1998**, *37*, 6281−6287.
[16] Heterolytic cleavage of hydrogen by Pd complexes has been proposed before: K. Kaneda, T. Manaka, *Trends Org. Chem.* **1991**, *2*, 109. This is reinforced from our experiments using more polar and protic acid media, which show a significant increase in reaction rate, probably resulting from charge separation during the formation of intermediate species (more detailed studies for establishing reaction pathways are in progress).
[17] [17a] M. S. Newman, S. I. Kosak, *J. Org. Chem.* **1949**, *14*, 375−381. [17b] T. A. Thornton, G. A. Ross, D. Patil, K. Mukaida, J. O Warnick, N. F. Woolsey, D. E Bartak, *J. Am. Chem. Soc.* **1989**, *111*, 2434−2440.
[18] [18a] M. Jun, C. Liu, *J. Coord. Chem.* **1975**, *5*, 1. [18b] M Jun, C. Liu, *Inorg. Chem.* **1975**, *14*, 2310−2314. [18c] A. Corma, M. Iglesias, C. del Pino, F. Sánchez, *J. Organomet. Chem.* **1992**, *431*, 233−246. [18d] A. Carmona, A. Corma, M. Iglesias, F. Sánchez, *Inorg. Chim. Acta* **1996**, *244*, 79−85. [18e] A. Carmona, A. Corma, M. Iglesias, F. Sánchez, *Inorg. Chim. Acta* **1996**, *244*, 239−245.
[19] E. Miranda, F. Sánchez, J. Sanz, M. I. Jiménez, I. Martínez-Castro, *J. High-Resol. Chromatogr.* **1998**, *21*, 225−233.
[20] G. M. Sheldrick, *SHELXTL program for the refinement of crystal structures*, University of Göttingen, Germany, **1997.**

Received September 5, 2003
Early View Article
Published Online March 31, 2004

