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Binaphthyl Schiff base complexes of palladium(II). Structures and reactivities toward alkene epoxidation

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Palladium(II) binaphthyl Schiff base complexes [Pd^{II}(L)] (**1**: H_2L = (racemic or *R*)-2,2′-bis(3,5-dichloro-2-hydroxybenzylideneamino)-1,1′-binaphthyl (H_2L^2); **2**: H_2L = (*R*)-2,2′-bis(3,5-dichloro-2-hydroxylbenzylideneamino)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (H_2L^3)) were prepared from sequential reactions of H_2L with sodium methoxide and palladium(II) acetate in methanol in about 70% yields. Both complexes **1** and **2** have been characterised by X-ray crystallography as well as ^{1}H NMR, IR, UV/VIS and MS spectroscopy. The structures of **1** and **2** feature a pseudo planar N_2O_2 arrangement with the Schiff base ligands adopting a stepped conformation, in contrast to the non-planar N_2O_2 geometry usually observed for this type of Schiff base bound to various metal ions. The catalytic behaviour of complexes **1** and **2** toward asymmetric epoxidation of styrenes was investigated. With **2** as a catalyst, a 71% ee was obtained for the epoxidation of *p*-fluorostyrene by ^{t}BuOOH.

Introduction

The C_2-symmetric 1,1-binaphthyl unit[1–3] and tetradentate Schiff bases (salen)[4–8] constitute two of the most important types of chiral auxiliaries in metal-mediated asymmetric catalysis. Recently, their "hybridized" forms, *i.e.* binaphthyl Schiff bases L^1 and L^2 (Fig. 1), have been developed.[5,9–11] The utility of L^1 in asymmetric catalysis has been a subject of much investigation.[5,12–25] In contrast, there are only a handful of reports on employing L^2 as a chiral auxiliary in asymmetric catalysis.[9–11,26–29] Nishinaga and co-workers reported that a Co–L^2 catalyst gave considerably higher enantioselectivity than its salen analogue in the oxygenation of styrene to form 1-phenylethanol.[9] Our recent work demonstrated that a Ti–L^2 complex catalyzes the trimethylsilylcyanation of aromatic aldehydes with up to 96% enantiomeric excess (ee)[26] but the epoxidation of unfunctionalized alkenes catalyzed by a Mn–L^2 complex[28] gives rise to lower ee's than by Mn–salen catalysts.

In the course of understanding the chiral induction by metal complexes bearing tetradentate Schiff bases, it is crucial to ascertain the coordination modes of these ligands. Salens are known to bind metal ions usually with a planar N_2O_2 geometry (inset (a) in Fig. 1), and are often reported to adopt a stepped conformation (inset (b) in Fig. 1).[30–32] These features remain

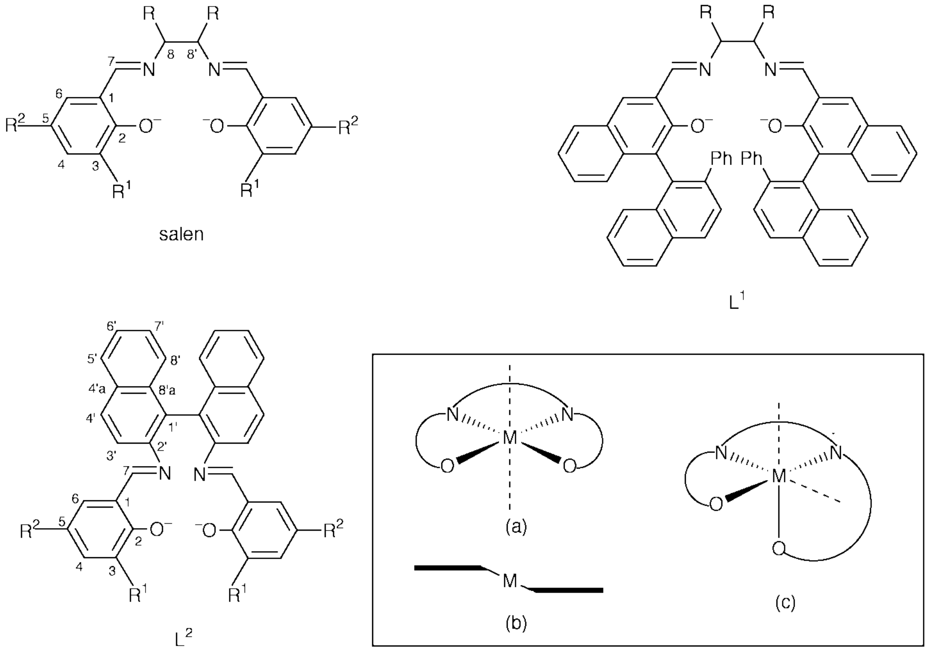


Fig. 1 Tetradentate Schiff base salen and its binaphthyl analogues L^1 and L^2. The inset shows the coordination modes (a and c) observed for these ligands in octahedral metal complexes and the stepped conformation (b) in (a). Note that all the metal complexes with the ligand L^2 appearing in this work have $R^1 = R^2 = Cl$.

unchanged upon "merging" the salen phenyl rings with binaphthyl units to form L^1.[5] The planar N_2O_2 arrangements,[4,33,34] or especially the stepped conformations,[5] of salen and L^1 are considered as the basis for accounting for the related chiral induction. "Merging" salen with the binaphthyl unit in the C8–C8′ bond region to form L^2, however, was found to change its coordination behaviour, as revealed by the structural determinations of metal complexes with L^2, in which the Schiff base ligand exclusively adopts a non-planar N_2O_2 arrangement with a helical conformation (inset (c) in Fig. 1).[26–28] These differences in coordination modes might be responsible for the above-mentioned lower chiral induction by Mn–L^2 than by Mn–salen catalysts.

In this work, it is our intention to (i) unearth the reasons why L^2 favours the non-planar N_2O_2 arrangement in binding metal ions and (ii) examine the catalytic properties of a metal–L^2 complex, $[Pd^{II}(L^2)]$ (**1**, $R^1 = R^2 = Cl$), that has a stepped conformation similar to salen and L^1 analogues. The synthesis, structure and catalytic properties of $[Pd^{II}(L^3)]$ (**2**, L^3 is a partially hydrogenated L^2, see Scheme 1), are also described. Prior to this work, only one palladium(II) tetradentate Schiff base complex was characterized by X-ray crystallography,[35] which contains N_3O rather than N_2O_2 chelating atoms. In addition, the present work provides the first asymmetric epoxidation of alkenes catalyzed by a palladium complex.

Experimental

General

^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 FT-NMR spectrometer (300 MHz). ^1H–^1H COSY and NOESY NMR spectra were recorded on a Bruker DRX 500 FT-NMR spectrometer (500 MHz). The chemical shifts (δ) are reported relative to tetramethylsilane (TMS). UV/VIS spectra were measured on a Perkin-Elmer Lambda 19 spectrophotometer. Infrared spectra were recorded on a Shimadzu-470 spectrometer. FAB and electrospray (ES) mass spectra were obtained on Finnigan MAT 95 and LCQ quadruple ion trap spectrometers, respectively. GC analyses were carried out on a HP 5890 series II system equipped with a HP 5890A flame ionisation detector and a HP 3395 integrator. Capillary columns β- (30 m × 0.25 mm) and γ-cyclodextrin (30 m × 0.32 mm) were used to analyse the epoxides. Elemental analyses were performed by the Institute of Chemistry, the Chinese Academy of Sciences. All solvents and substrates were purified by standard procedures. *tert*-Butyl hydroperoxide (TBHP) in toluene was prepared by the method of Sharpless.[36] The binaphthyl Schiff bases H_2L^2 and H_2L^3 were prepared according to the published procedures.[10,11,26]

Preparation of $[Pd^{II}(L^2)]$ (1) and $[Pd^{II}(L^3)]$ (2)

To a mixture of Schiff base H_2L^2 (125 mg, 0.27 mmol) or H_2L^3 (127 mg, 0.27 mmol) and NaOMe (35 mg, 0.65 mmol) in methanol (20 mL) was added palladium(II) acetate (61 mg, 0.27 mmol). After the mixture was stirred for 2 h, a yellow precipitate was formed. The precipitate was collected by filtration, washed with methanol and ether, and dried in air.

$[Pd^{II}(L^2)]$ (1). The racemic and chiral (*R*-configuration) complexes of **1** were prepared in *ca.* 76% yields by employing racemic H_2L^2 and (*R*)-H_2L^2, respectively. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.01 (d, $J = 8.58$ Hz, 2H, 4′-H), 7.97 (d, $J = 8.21$ Hz, 2H, 8′-H), 7.61–7.53 (m, 2H, 7′-H), 7.40 (d, $J = 2.62$ Hz, 2H, 4-H), 7.34 (s, 2H, 7-H), 7.31–7.28 (m, 2H, 6′-H), 7.13 (d, $J = 8.55$ Hz, 2H, 3′-H), 6.99 (d, $J = 2.63$ Hz, 2H, 6-H), 6.96 (d, $J = 8.52$ Hz, 2H, 5′-H). IR (KBr, cm^{-1}): 1603, 1507, 1430, 1169, 949, 864, 821, 801, 774, 748, 488. UV/VIS ($CHCl_3$): λ_{max}/nm ($\varepsilon \times 10^{-4}$/$dm^3$ mol^{-1} cm^{-1}) 265 (4.93) sh, 283 (3.20) sh, 318 (1.70) sh, 441 (0.67). FAB MS: *m*/*z* 735 (M^+) (Found: C, 53.86; H, 2.82; N, 3.45. $C_{34}H_{18}Cl_4N_2O_2Pd\cdot H_2O$ requires C, 54.26; H, 2.66; N, 3.72%).

$[Pd^{II}(L^3)]$ (2). Yield: 65%. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.40 (d, $J = 2.65$ Hz, 2H, 4-H), 7.29 (s, 2H, 7-H), 7.09 (d, $J = 8.71$ Hz, 2H), 7.08 (d, $J = 2.75$ Hz, 2H, 6-H), 6.66 (d, $J = 7.96$ Hz, 2H), 2.83–1.60 (m, 16H, CH_2). IR (KBr, cm^{-1}): 1607, 1511, 1430, 1304, 1200, 1169, 761. UV/VIS ($CHCl_3$): λ_{max}/nm ($\varepsilon \times 10^{-4}$/$dm^3$ mol^{-1} cm^{-1}) 258 (5.89) sh, 296 (2.78) sh, 445 (1.01). FAB MS: *m*/*z* 743 (M^+) (Found: C, 53.89; H, 3.57; N, 4.02. $C_{34}H_{26}Cl_4N_2O_2Pd\cdot 0.5H_2O$ requires C, 54.33; H, 3.60; N, 3.73%).

X-Ray structural determinations

Single crystals of H_2L^3 were grown by vapour diffusion of pentane into a solution of H_2L^3 in chloroform. Single crystals of complexes $\mathbf{1}\cdot 0.5CH_2Cl_2$ and $\mathbf{2}\cdot$AcOEt were obtained by laying *n*-hexane on the top of a solution of racemic **1** in dichloromethane and by vapour diffusion of hexane into a solution of **2** in ethyl acetate. Data were collected on a Rigaku RAXIS-IIC imaging-plate diffractometer (H_2L^3 and $\mathbf{2}\cdot$AcOEt) and a Siemens P4 four-circle diffractometer ($\mathbf{1}\cdot 0.5CH_2Cl_2$), both with a Mo-Kα source ($\lambda = 0.71073$ Å). For $\mathbf{1}\cdot 0.5CH_2Cl_2$, the XSCANS program (Siemens Reference Manual) was applied to search for diffraction peaks to determine cell parameters, data collection and reduction. The crystallographic data were corrected using the LP factor and semi-empirical absorption corrections were also applied. For H_2L^3 and $\mathbf{2}\cdot$AcOEt, data collections were made with 3° oscillation (60 images) at 12 cm distance and 8 min exposure. Absorption corrections were made by using the ABSCOR program.[37] All calculations were performed on a PC 486 computer with the SHELXTL-PC program package.[38] The structure was solved by direct methods for H_2L^3, and by the Patterson superposition method for $\mathbf{1}\cdot 0.5CH_2Cl_2$ and $\mathbf{2}\cdot$AcOEt. Conventional *R*-factors R_1 and weighted *R*-factors wR_2 are based on F and F^2, respectively. In all cases, the non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method, whereas hydrogen atoms were placed in calculated positions (C–H 0.96 Å), assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms.

CCDC reference number 186/1833.

See http://www.rsc.org/suppdata/dt/a9/a908917i/ for crystallographic files in .cif format.

Asymmetric epoxidation of alkenes catalysed by complexes 1 and 2

A typical procedure. To a mixture of activated 4 Å molecular sieves (200 mg, Aldrich) and complex **1** or **2** (0.01 mmol) in dry toluene (4 mL) was added styrene (0.05 mmol). Upon cooling to 0 °C, a 3.1 M solution of TBHP in toluene (66.7 μL, 0.2 mmol) was added. The mixture was stirred at 0 °C for 6 h, and then chromatographed on silica gel with ethyl acetate–*n*-hexane (1 : 6) as the eluant. The yield and ee of the products were determined by GC.

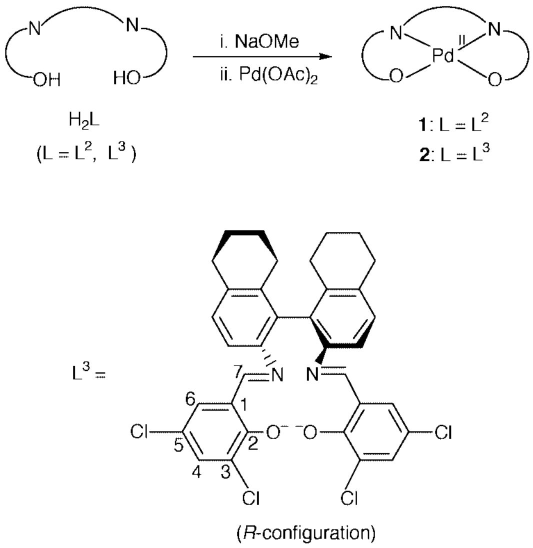
Results and discussion

There are a variety of palladium(II) Schiff base complexes known in the literature, of which only those bearing bidentate Schiff base ligands are well documented.[39] Although a Pd(II)-salen complex was first isolated in 1963,[40] tetradentate Schiff base complexes of this metal ion are still sparse.[35,39–42] In this work, sequential treatment of H_2L^2 or H_2L^3 with sodium methoxide and palladium(II) acetate in methanol readily afforded complex **1** or **2** as a pale yellow precipitate (Scheme 1). By washing with methanol and ether, analytically pure products of **1** and **2** were obtained in about 70% yields.

Table 1 Crystallographic data for H_2L^3, $[Pd^{II}(L^2)]$ (**1**) and $[Pd^{II}(L^3)]$ (**2**)

	H_2L^3	**1**·$0.5CH_2Cl_2$	**2**·AcOEt
Chemical formula	$C_{34}H_{28}Cl_4N_2O_2$	$C_{34}H_{18}Cl_4N_2O_2Pd\cdot 0.5CH_2Cl_2$	$C_{34}H_{26}Cl_4N_2O_2Pd\cdot AcOEt$
Formula weight	638.38	777.17	830.87
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a/Å	22.530(5)	10.359(2)	10.317(2)
b/Å	10.765(2)	13.218(3)	13.332(3)
c/Å	12.843(3)	14.597(3)	13.668(3)
a/°		63.28(3)	98.88(3)
β/°	91.78(3)	71.03(3)	93.85(3)
γ/°		75.74(3)	102.00(3)
V/Å^3	3113.5(11)	1676.4(6)	1807.3(6)
Z	4	2	2
T/K	293(2)	293(2)	293(2)
λ/Å	0.71073	0.71073	0.71073
ρ_{calc}/g cm^{-3}	1.362	1.540	1.527
μ/mm^{-1}	0.414	0.986	0.852
$R_1{}^a$ ($I > 2\sigma(I)$)	0.047	0.07	0.079
$wR_2{}^b$ ($I > 2\sigma(I)$)	0.15	0.19	0.18

^{a} $R_1 = \Sigma||F_o| - |F_c||/|F_c|$. ^{b} $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.



Scheme 1

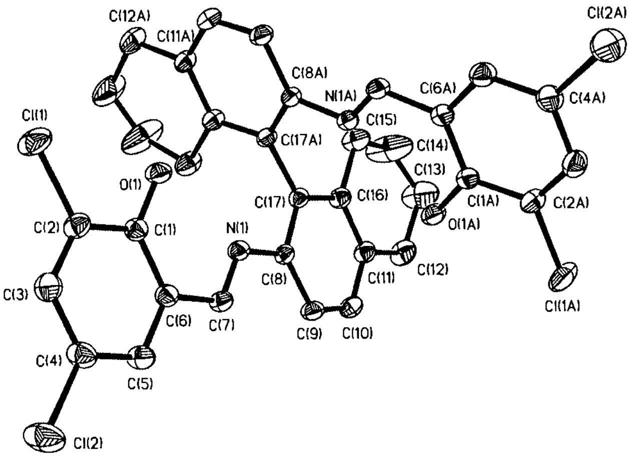


Fig. 2 ORTEP[57] drawing with the atom-numbering scheme for H_2L^3 (35% probability ellipsoids). Hydrogen atoms are omitted for clarity.

Spectral features of complexes 1 and 2

Complexes **1** and **2** are diamagnetic, exhibiting well-resolved ^1H NMR signals of the coordinated Schiff bases at normal fields. In each case, only one set of naphthyl or benzylideneamine proton resonances has been observed, suggesting that both **1** and **2** have a C_2 symmetry in solution. The signal assignment for **1** was made on the basis of ^1H–^1H COSY and NOESY NMR measurements. The spectrum of complex **2** is more complicated, featuring several multiplets in the aliphatic region. However, the 4-, 6-, and 7-H chemical shifts are similar to those observed for complex **1**. Compared with H_2L^2 and H_2L^3, which give 7-H resonances at 8.55[27] and 8.4[26] ppm, respectively, both **1** and **2** exhibit the 7-H signals (7.34 and 7.29 ppm, respectively) upfield shifted by more than 1.1 ppm. For comparison, binding of L^2 to a ruthenium(II) ion to form the diamagnetic complex $[Ru^{II}(L^2)(NO)Cl]$[26] shifts the 7-H signal upfield by less than 0.74 ppm.

A comparison of the UV/VIS spectra between **1** and H_2L^2 or between **2** and H_2L^3 showed that both ligands lost almost all the original bands upon binding to the palladium(II) ion, indicating the occurrence of a major structure adjustment, such as a severe breakage of the π-electron delocalization over the entire halves of L^2 or L^3 (*vide infra*). The IR spectra of **1** and **2** exhibit intense bands at 1603 and 1607 cm^{-1}, respectively, ascribable to the C=N stretching vibrations. In the FAB MS measurements, the cluster peak of the parent ion for either **1** (m/z = 735) or **2** (m/z = 743) was observed.

Structure determinations of H_2L^3, $[Pd^{II}(L^2)]$ (1) and $[Pd^{II}(L^3)]$ (2)

Table 1 summarises the crystallographic data for the three compounds, whose structures are shown in Fig. 2–4. Selected bond distances and angles are listed in Table 2.

The compound H_2L^3 (Fig. 2) is the first structurally characterised example of partially hydrogenated H_2L^2. The component atoms of each half of H_2L^3 are basically co-planar (mean deviation from the least-squares plane: 0.0637 Å), with the least-squares planes of the two halves making a dihedral angle of 85.9°. These features are similar to those observed for H_2L^2 by Meunier and co-workers.[10] However, partial hydrogenation of H_2L^2 does cause some appreciable structural changes. For example, for the partially hydrogenated naphthyl groups in H_2L^3, the bond distances involving the sp^3 carbon atoms average 1.460(3) Å, which is significantly longer than the mean distance (1.392(2) Å) between the sp^2 carbon atoms; the angles C(11)–C(12)–C(13) and C(14)–C(15)–C(16) of 114.0(2)° are considerably smaller than the angles (120°) expected in an idealized phenyl ring.

The unit cell of racemic complex **1** consists of a pair of (*R*)- and (*S*)-enantiomers, whose structures feature an almost planar N_2O_2 arrangement (Fig. 3) with a mean deviation of 0.11 Å from the least-squares plane. This is different from the structures of $[Cu^{II}(L^2)]$,[27] $[M^{III}(L^2)(acac)]$ (M = Fe, Mn),[28] and $[Ru^{II}(L^2)(NO)Cl]$[26] with the same ligand, all of which have a

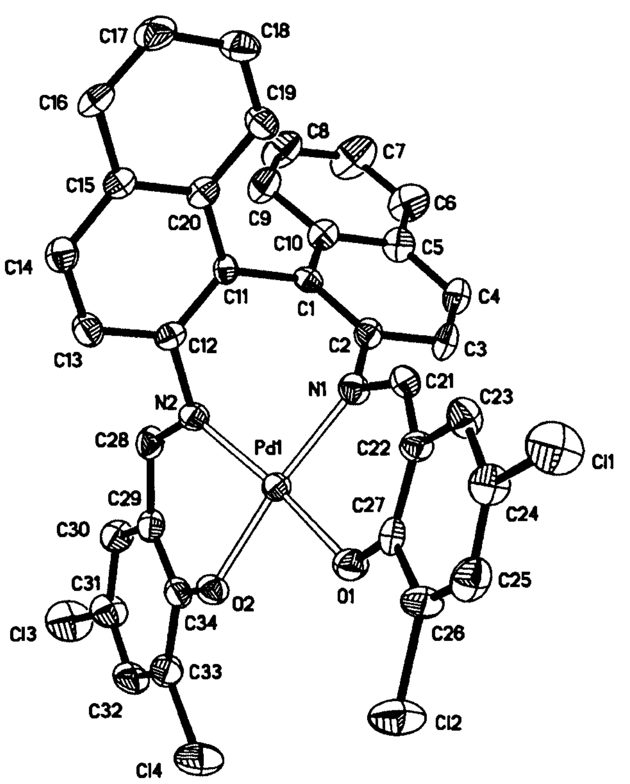


Fig. 3 ORTEP drawing with the atom-numbering scheme for the (*R*)-enantiomer of complex **1** (35% probability ellipsoids). Hydrogen atoms are omitted for clarity.

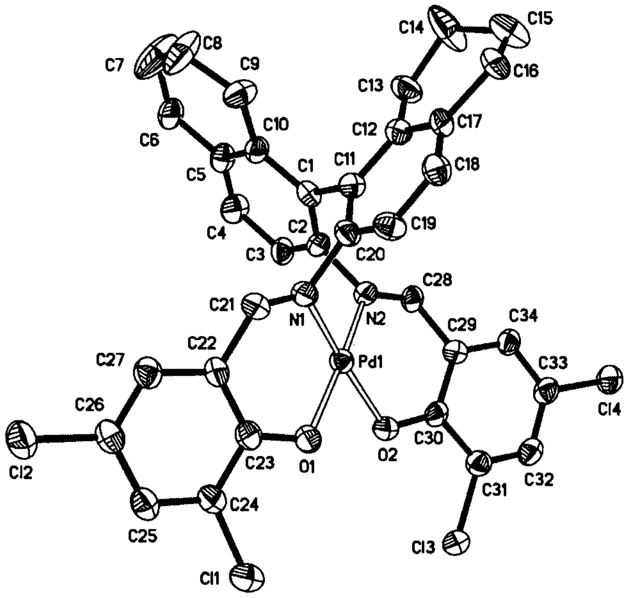


Fig. 4 ORTEP drawing with the atom-numbering scheme for complex **2** (35% probability ellipsoids). Hydrogen atoms are omitted for clarity.

non-planar N_2O_2 geometry as shown in inset (c) of Fig. 1, except for $[Cu^{II}(L^2)]$ having a typical distorted tetrahedral N_2O_2 arrangement. The structure of the chiral complex **2** (Fig. 4) resembles that of complex **1**, which again features an almost planar N_2O_2 geometry, with the mean deviation from the least-squares plane of 0.12 Å. The bond distances involving the sp^3 carbon atoms of the partially hydrogenated naphthyl groups average 1.486(5) Å, similar to the mean value of these distances found in H_2L^3.

Rationalisation of the coordination behaviour of L^2 or L^3

Table 2 Selected bond distances (Å) and angles (°) for H_2L^3, $[Pd^{II}(L^2)]$ (**1**), and $[Pd^{II}(L^3)]$ (**2**)

H_2L^3			
C(11)–C(12)	1.512(2)	C(12)–C(13)	1.481(3)
C(13)–C(14)	1.312(3)	C(14)–C(15)	1.475(3)
C(15)–C(16)	1.520(2)	C(11)–C(16)	1.399(2)
C(17)–C(17A)	1.505(3)	C(7)–N(1)	1.279(2)
C(8)–N(1)	1.415(2)	C(2)–Cl(1)	1.733(2)
C(12)–C(11)–C(16)	121.4(2)	C(15)–C(16)–C(11)	120.5(1)
C(11)–C(12)–C(13)	114.0(2)	C(12)–C(13)–C(14)	121.7(2)
C(13)–C(14)–C(15)	123.0(3)	C(14)–C(15)–C(16)	114.0(2)
C(13)–C(12)–C(17)	121.6(2)	C(12)–C(17)–C(16)	121.5(2)
$[Pd^{II}(L^2)]$ (**1**)			
Pd(1)–N(1)	1.975(3)	N(1)–C(21)	1.302(4)
Pd(1)–N(2)	1.989(3)	N(2)–C(28)	1.291(4)
Pd(1)–O(1)	2.004(3)	C(27)–O(1)	1.299(4)
Pd(1)–O(2)	1.990(2)	C(34)–O(2)	1.300(4)
N(1)–Pd(1)–N(2)	94.1(1)	O(2)–Pd(1)–O(1)	86.7(1)
N(2)–Pd(1)–O(2)	89.9(1)	N(1)–Pd(1)–O(1)	89.9(1)
Pd(1)–O(1)–C(27)	120.9(2)	Pd(1)–O(2)–C(34)	121.5(2)
Pd(1)–N(1)–C(2)	116.9(2)	Pd(1)–N(1)–C(21)	124.0(2)
Pd(1)–N(2)–C(12)	117.5(2)	Pd(1)–N(2)–C(28)	125.3(3)
$[Pd^{II}(L^3)]$ (**2**)			
Pd(1)–N(1)	2.006(2)	N(1)–C(21)	1.249(3)
Pd(1)–N(2)	1.993(2)	N(2)–C(28)	1.280(3)
Pd(1)–O(1)	2.000(2)	C(23)–O(1)	1.294(3)
Pd(1)–O(2)	1.998(2)	C(30)–O(2)	1.285(3)
N(1)–Pd(1)–N(2)	94.46(7)	O(1)–Pd(1)–O(2)	86.97(6)
N(1)–Pd(1)–O(1)	89.41(7)	O(2)–Pd(1)–N(2)	90.05(7)
Pd(1)–O(1)–C(23)	120.4(1)	Pd(1)–O(2)–C(30)	121.1(1)
Pd(1)–N(1)–C(20)	114.5(1)	Pd(1)–N(1)–C(21)	124.3(1)
Pd(1)–N(2)–C(2)	115.6(1)	Pd(1)–N(2)–C(28)	124.3(1)

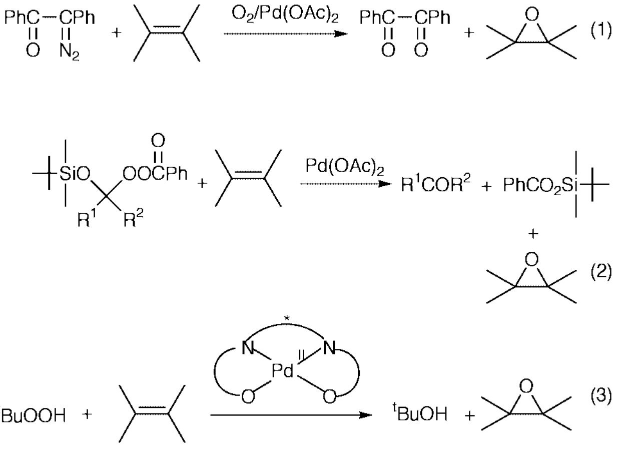
Although the non-planar N_2O_2 geometry in the structures of $[M^{III}(L^2)(acac)]$ (M = Fe, Mn),[28] both bearing an extra bidentate acac ligand, does not unquestionably signify an unusual coordination behaviour of L^2 as compared to salen,[43] such a geometry found for $[Cu^{II}(L^2)]$[27] and $[Ru^{II}(L^2)(NO)Cl]$[26] suggests that the binaphthyl Schiff base L^2 is different from salen in chelating metal ions, since both $[Cu^{II}(salen)]$[44] and $[Ru^{II}(salen)(NO)Cl]$[45,46] have been found to adopt basically planar N_2O_2 arrangements. The questions naturally arise as to what causes such a difference and why complexes **1** and **2** show an almost planar N_2O_2 geometry. To address the first question, the following possibilities are to be considered: (i) the σ-bonds linking naphthyl and phenoxide rings might experience a significantly larger strain when L^2 adopts a planar N_2O_2 arrangement; (ii) the rigidity of the binaphthyl unit,[3] *i.e.* the propensity of two naphthyl planes to maintain a relatively large dihedral angle, possibly makes it hard for L^2 to accommodate a planar N_2O_2 geometry; and (iii) the propensity of the π-electrons in L^2 to have maximum delocalisation may favour the non-planar N_2O_2 geometry. It seems that the possibilities (i) and (ii) could be excluded, since the key bond distances and angles, and the binaphthyl dihedral angles of L^2 or L^3 in the complexes with planar and non-planar N_2O_2 moieties are found to be similar.

The dihedral angles between benzylideneamine and the attached naphthyl plane in complexes **1** and **2** were then examined, which are *ca.* 93 and 91°, respectively, both considerably larger than the corresponding angles found in the complex $[Ru^{II}(L^2)(NO)(Cl)]$ with non-planar N_2O_2 geometry (64°).[26] This indicates that maintaining a pseudo planar N_2O_2 coordination mode would almost fully break the π-electron delocalisation from benzylideneamine to the attached naphthyl groups, causing L^2 or L^3 to suffer from a significant strain. Therefore, the propensity for the π-electrons in L^2 to have maximum delocalisation seems to favour the non-planar N_2O_2 geometry.

The pseudo planar N_2O_2 geometry observed for complexes **1** and **2** could be rationalised by a strong preference of the palladium(II) ion for a square planar configuration.[39,47,48] It is likely that the enhanced stability resulting from the pseudo square planar coordination of the palladium(II) ion to L^2 or L^3 compensates the strain due mainly to forcing the benzylideneamine planes to be almost perpendicular to the attached naphthyl rings. Interestingly, either complex **1** or **2** adopts a typical stepped conformation, like metal–salen[30–32] and metal–L^1[5] complexes. The phenoxide rings of **1** or **2** constitute a dihedral angle of 10.3 or 10.6°, respectively, both smaller than the corresponding angle of 17.3° found in $[Cr^{III}(salen)(H_2O)_2]Cl$.[49]

Alkene epoxidation catalyzed by complexes 1 and 2

Palladium-mediated catalysis in organic synthesis has received much attention.[50,51] Nevertheless, there are only two reports in the literature on alkene epoxidation catalyzed by palladium complexes,[52,53] neither is enantioselective. In 1980, Foote and Ryang reported that $PhC(O)C(N_2)Ph$ reacted readily with oxygen in the presence of palladium(II) acetate to give an intermediate which can transfer an oxygen atom to alkenes to give epoxides under very mild conditions (reaction 1 in Scheme 2).[52]



Scheme 2

Thereafter, Saito and co-workers observed that reaction of alkenes with α-silyloxyalkyl peroxybenzoates in the presence of palladium(II) acetate also afforded epoxide products (reaction 2 in Scheme 2).[53] Noticeably, although a number of palladium Schiff base complexes have been reported,[35,39–42] their reactivity toward alkene epoxidation remains unexplored.

We investigated the reactions of styrene and substituted styrenes with several oxidants, namely TBHP, PhIO[54a] and Cl_2-PyNO (2,6-dichloropyridine *N*-oxide), in dichloromethane or toluene in the presence of a catalytic amount of chiral complexes **1** or **2**. Cl_2PyNO was found to be unreactive toward the epoxidation reactions. In the case of PhIO, severe degradation of the catalysts occurred, and the yields of epoxides were very low. For example, with a **1** : PhIO : styrene molar ratio of 1 : 10 : 50, only <8% yield of styrene oxide (based on the amount of starting PhIO) was obtained after a 6 h reaction in toluene. The oxidation by TBHP (reaction 3 in Scheme 2) afforded epoxides in better yields (*vide infra*), although catalyst degradation was still a problem. The major side products were aldehydes. This is different from the reactions between terminal alkenes (such as cyclohexene and styrene) and $Pd(RCO_2)$-(Bu^tOO) (obtained by treating $Pd(RCO_2)_2$ with TBHP) reported by Mimoun and co-workers,[54b] which resulted in the formation of methyl ketones in ≥98% yields. Preliminary studies revealed that complex **2**, bearing the partially-hydrogenated binaphthyl Schiff base, is superior to complex **1** as the epoxidation catalyst, and toluene is a better solvent than dichloromethane. The results described below were all obtained in toluene.

With a catalyst : styrene : TBHP molar ratio of 1 : 5 : 20, reaction 3 catalysed by complex **2** gave rise to a 16% conversion of styrene after 6 h, affording styrene epoxide and benzaldehyde in 37 and 50% yield (based on the consumed styrene), respectively, with a 17% ee obtained for the epoxide. Under the same conditions except with *p*-fluorostyrene as substrate, a 27% conversion, 51 and 32% yields of *p*-fluorostyrene epoxide and *p*-fluorobenzaldehyde, respectively, were obtained, with the ee of the epoxide reaching 71%. This is to be compared with the $[Cu^{II}(L^2)]$/TBHP system,[27] which affords epoxides in moderate yields but gives no asymmetric induction. Since complex $[Cu^{II}(L^2)]$ has a typical distorted tetrahedral N_2O_2 arrangement with a helical conformation, it might be the case that the stepped conformations of catalysts **1** and **2** are indeed beneficial to the chiral induction.

Worthy of note is that *p*-methylstyrene, which has an electron-donating *para* substituent, was almost unreactive toward reaction 3 (<2% conversion after a 6 h reaction). This, together with the results described above, probably suggests that a less electron-rich alkene is more reactive toward reaction 3, a feature to some extent similar to the alkene epoxidations by metalloporphyrin peroxo complexes reported by Valentine and co-workers.[55,56] The epoxidations of *cis*- and *trans*-β-methylstyrene *via* reaction 3 resulted in poor enantioselectivity (<5% ee), and were non-stereospecific for the *cis* alkene, like the epoxidation of *cis* alkenes through reactions 1 and 2. This implies that a stepwise mechanism is operative in the case of this substrate.

In attempting to identify the active intermediates in reaction 3, we treated complex **1** with 20 equiv. of TBHP, a molar ratio identical to that for the catalytic reactions, in dichloromethane at room temperature for 0.5 h and obtained a homogeneous solution. The ES-MS of the solution shows a peak at *m/z* 735 corresponding to the parent ion of complex **1** and a more intense peak at *m/z* 823 which could be ascribed to $[Pd(L^2)(OOBu^t)]^+$ or $\{[Pd(L^2)(HOOBu^t)] - H\}^+$. No peaks due to demetallation were observed under the ES-MS conditions.

Conclusions

Palladium(II) tetradentate binaphthyl Schiff base complexes, $[Pd^{II}(L^2)]$ (**1**) and $[Pd^{II}(L^3)]$ (**2**), could be readily prepared through reaction of palladium(II) acetate with sodium methoxide-treated H_2L^2 and H_2L^3, respectively. Both complexes have a pseudo planar N_2O_2 arrangement with the ligands adopting a typical stepped conformation, a coordination mode unusual for metal–L^2 complexes but attributable to the strong preference of palladium(II) ion for a square planar geometry. Comparison of the key metrical parameters of **1** and **2** with those of related metal complexes having the usual non-planar N_2O_2 arrangements reveals that the propensity of the π-electrons in L^2, and L^3 as well, to have maximum delocalisation is most probably a dominant factor in controlling the coordination mode of such Schiff bases. The chiral complexes **1** and **2** can catalyse the asymmetric epoxidation of unfunctionalised alkenes with up to 71% ee.

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