

Ruthenium(II) complexes with 2,6-pyridyl-diimine ligands: synthesis, characterization and catalytic activity in epoxidation reactions

Bekir Çetinkaya^{a,*}, Engin Çetinkaya^b, Maurice Brookhart^c, Peter S. White^{c,1}

^a Department of Chemistry, Ege University, Izmir, Turkey

^b Department of Chemistry, İnönü University, Malatya, Turkey

^c Department of Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3290, USA

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Abstract

Reaction of $[\text{RuCl}_2(p\text{-cymene})]_2$ with the tridentate $N\text{-}N'\text{-}N$ ligands, 2,6-pyridyl-diimines, led to substitution of $p\text{-cymene}$. The resulting complexes, believed to be coordinatively unsaturated, exhibit efficient activity for the epoxidation of cyclohexene in the presence of iodosobenzene (PhIO): the complexes formed initially take up donor molecules such as acetonitrile to achieve hexacoordination. The molecular structure for one of these, (acetonitrile){2,6-bis[1-(4-methoxyphenylimino)ethyl]pyridine}dichlororuthenium(II), **2**, has been determined by X-ray diffraction. The immediate coordination sphere is a distorted octahedron with *trans* chloride atoms and a short Ru–N(py) (1.906 Å) bond. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Pyridine-2,6-diimines; Ruthenium(II) complexes; Epoxidation catalysts; Epoxidation of cyclohexene; X-ray structure of Ru(II)

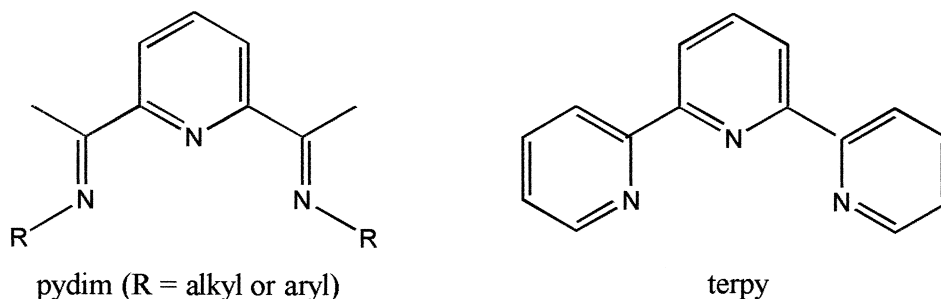
1. Introduction

There is great current interest in pyridine-based tridentate ligands. This is primarily due to their stability under a variety of oxidative and reductive conditions and the fact that pyridine ligands are on the borderline between hard and soft Lewis bases. Examples of such ligands include the well-known 2,2':6',2''-terpyridine (terpy) [1–4], pyridylbisamines [5,6], pyridylbisamides [7], pyridylbisoxazolines (pybox) [8–12], pyridylbispyrazolines [13] and pyridylbispyrimidines [14]. In this context, 2,6-pyridyl-diimines (pydim) [15,16] have emerged as an alternative to terpy. In virtually all of the complexes prepared to date (e.g., five-coordinate $[\text{MX}_2(\text{pydim})]$ (M = Mn, Fe, Co, Ni, Cu, Zn, Cd; X = Cl, Br) and six-coordinate $[\text{M}(\text{pydim})_2]\text{X}_2$ (X = BF_4 , ClO_4 ; not all combinations)) the pydim

* Corresponding author. E-mail: cetikaya@fenfak2.ege.edu.tr

¹ To whom correspondence concerning crystallographic studies should be addressed. E-mail: pwhite@pyrite.chem.unc.edu.

behaves as a tridentate ligand [17–25]. Pydim has been observed to function as a bidentate chelating ligand in certain carbonyl derivatives [26,27].



Pyridine ligands, substituted in the 2,6-positions with a variety of chiral groups bearing coordinating nitrogen atoms, capable of forming chelates with ruthenium(II) have been prepared and investigated in catalytic applications [9–12]. We are not aware of any previous reports of reactions of Ru(II)–pydim complexes. Thus, it was the goal of this work to prepare well-defined Ru(II) catalyst precursors incorporating pydim ligands for alkene epoxidation.

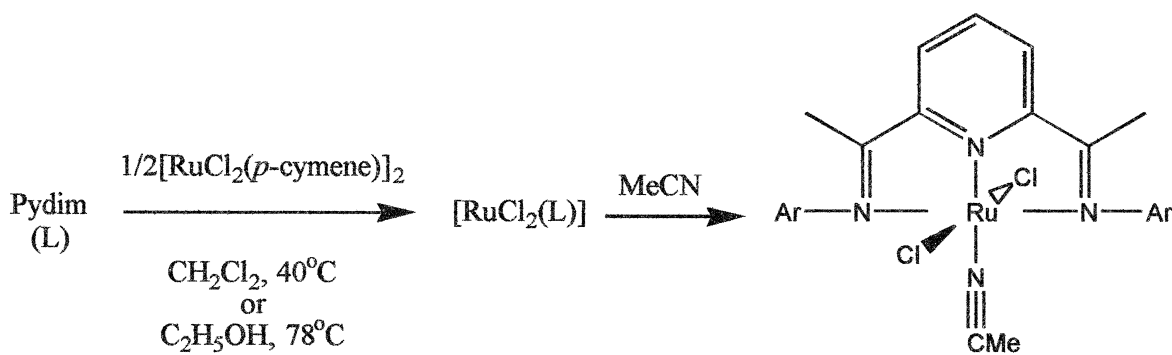
2. Results and discussion

2.1. Synthesis and characterization of ligands and ruthenium complexes

The tridentate (*N-N'-N*) pydim ligands (L) were prepared via condensation of commercially available 2,6-diacetylpyridine with two molar equivalents of the corresponding aniline. Ligands L¹ and L² have been reported previously [17], ligands L³–L⁷ were prepared by the same procedure, but with minor modification and identified via microanalytical and NMR data.

Complexation of pydims with 0.5 equivalent of [RuCl₂(*p*-cymene)]₂ in boiling dichloromethane resulted in deep-purple solutions (Scheme 1). The choice of reaction solvent proved to be quite important. Thus, in the case of ligands bearing *ortho*-substituted aryl groups (L⁴–L⁶) the complexation reactions were not complete, even in boiling 1,2-dichloroethane (DCE). However, ethanol was found to be a satisfactory solvent for these syntheses. The '[RuCl₂L]' products obtained from these mixtures gave complex and often variable ¹H NMR spectra: this property was attributed to the solvated molecules such as CH₂Cl₂ or C₂H₅OH which could partly be removed upon recrystallization or washing with pentane. Therefore, no attempt was made to fully characterize these products. However, they were used as epoxidation catalysts (*vide infra*). The [RuCl₂L] stoichiometry of these complexes was unequivocally established by trapping with two-electron donor ligands such as acetonitrile to achieve well-defined hexacoordinate complexes [RuCl₂L(NCCH₃)]. In this manner the compounds 1–7 were fully characterized via elemental analysis and NMR spectroscopy. ¹H NMR details for the ligands and complexes are presented in Table 1. ¹³C NMR and physical data are given in the Section 3.

The NMR spectra of the complexes were diagnostic. Only a single set of signals were observed for the two pendant groups of pydim complexes in both the ¹H and ¹³C NMR spectra which indicate that



L	Ar	
L ¹	4 - MeC ₆ H ₄	1
L ²	4 - MeOC ₆ H ₄	2
L ³	4 - Bu ^t C ₆ H ₄	3
L ⁴	2 - Bu ^t C ₆ H ₄	4
L ⁵	2,4 - Me ₂ C ₆ H ₃	5
L ⁶	2,6 - Me ₂ C ₆ H ₃	6
L ⁷	3,5 - Me ₂ C ₆ H ₃	7

Scheme 1.

the two 'arms' of the ligands are magnetically equivalent in solution and the ligands are tridentate (for atom labeling scheme see Fig. 1).

The effect of complexation on ¹H chemical shifts of the ligand is also informative. Attachment of the metal shifts the resonances of the pyridine hydrogens (AB₂ system) towards high field ($\Delta\delta_a$ 0.44–0.60) while all the ¹H resonances of the imine substituents move towards lower field ($\Delta\delta_c$ 0.24–0.32). The upfield shift of the pyridine resonances suggest significant backbonding from Ru(II) to the π^* orbitals of pyridine. The coordinated CH₃CN ligands show ¹H methyl resonances at higher frequencies relative to the free ligand. In general, the nitrile ligands are labile in all ruthenium complexes although complete substitution of these ligands does not occur readily [28–30].

The solid-state structure for the methoxy derivative was determined by X-ray diffraction. Details of the data collection are given in Table 2 and a list of selected bond lengths and bond angles are in Table 3. An ORTEP view of **2** is shown in Fig. 2. The immediate Ru coordination sphere is a distorted octahedron, with the major distortion arising via the N(4)–Ru–N(15) angle, at 158.7(3)°.

Table 1

¹H NMR data^{a,b} for the ligands (L)^c and the complexes (1–8)^d

Compound number	a	b	c	1	1'	2	2'	3	Others
L ¹	7.84t (7.8)	8.31d (8.0)	2.39s	7.17d (8.2)	7.17d (8.2)	6.74d (8.2)	6.74d (8.2)	2.35s	
1	7.59t (8.4)	7.83d (8.0)	2.73s	7.23d (8.7)	7.23d (8.7)	7.19d (8.4)	7.19d (8.4)	2.38s	2.07s ^e
L ²	7.83t (8.0)	8.30d (7.2)	2.41s	6.92d (7.7)	6.92d (7.7)	6.80d (7.7)	6.80d (7.7)	3.82s	f
2	7.60t (7.6)	7.82d (7.7)	2.74s	7.26d (9.1)	7.26d (9.1)	6.94d (9.1)	6.94d (9.1)	3.83s	2.14 ^e
L ³	7.83t (7.8)	8.31d (7.9)	2.41s	7.37d (8.6)	7.37d (8.6)	6.78d (8.5)	6.78d (8.5)	1.33s	
3	7.53t (8.0)	7.76d (7.8)	2.76s	7.36d (8.4)	7.36d (8.4)	7.15d (8.2)	7.15d (8.2)	1.40s	2.05s ^e 3.76s ^g
L ⁴	7.93t (7.8)	8.42d (8.0)	2.43s	1.38s	7.45dd (1.4, 7.4)	6.56dd (1.4, 7.4)	7.08dt (1.4, 7.4)	7.20dt (1.4, 7.4)	
4	7.65t (8.0)	7.78d (7.6)	2.63s	1.34s	7.55m ^h	7.55m ^h	7.20m ^h	7.20m ^h	1.99s ^e
L ⁵	7.88t (7.9)	8.40d (8.0)	2.34s	2.33s	7.00d (8.4)	7.08s	6.80d (8.4)	2.10s	
5	7.61t (8.1)	7.84d (7.8)	2.62s	2.32s	7.38dd (2.1, 7.8)	7.05s	7.01d (7.8)	2.16s	2.04s ^e 5.32 ^h
L ⁶	7.92t (7.8)	8.51d (8.0)	2.27s	2.08s	2.08s	7.10d (7.6)	7.10d (7.6)	6.97t (8.5)	
6	7.65t (7.4)	7.91d (8.4)	2.59s	2.23s	2.23s	7.09s	7.09s	7.09s	2.28s ^e 5.32 ^h
L ⁷	7.84t (7.8)	8.31d (7.8)	2.40s	6.47s	6.47s	2.33s	2.33s	6.76s	
7	7.59t (7.8)	7.82d (8.1)	2.72s	6.93s	6.93s	2.34s	2.34s	6.93s	2.10s ^e 5.32 ^h
8	7.35m ⁱ	j	2.38s	6.90m ⁱ	6.90m ⁱ	6.90m ⁱ	6.90m ⁱ	3.84s	6.7m ^{i,k} 7.1m ^{i,k}

^aFor labeling pydim protons see Fig. 1: the numbers represent arene or alkyl protons.^bChemical shifts (ppm) relative to residual CDCl₃ or CD₂Cl₂, coupling constants (J/Hz) given in parentheses.^cMeasured in CDCl₃.^dMeasured in CD₂Cl₂.^eDue to coordinated acetonitrile.^fTaken from Ref. [16].^gDue to solvated 1,2-dichloroethane (DCE).^hDue to solvated dichloromethane.ⁱTentative assignment, center of multiplet.^jMultiplet overlaps with the H_a resonances.^kDue to P–C₆H₅.

This angle is considerably smaller than the ideal angle of 180° and there is no steric barrier to coordination of a fourth ligand in the equatorial plane *trans* to the pyridine moiety.

The angle N(1)–Ru–N(12) involving the acetonitrile and the pyridine nitrogen, is normal at 179.1(3)°. Ru–N(1), Ru–N(4) and Ru–N(15) bond lengths are comparable to the reported values for [RuCl₂(pybox-dihydro)(C₂H₄)] [12]; however, the Ru–py (Ru–N(12)) bond length, 1.906(7) Å, is short and even shorter than the Ru–acetonitrile (Ru–N(1)) bond length. The phenyl rings are twisted; the angles between these two rings and the plane defined by the Ru and the four donor N-atoms are 54.78° and 68.58° for the 'a' and 'b' rings, respectively.

Ligands considerable bulkier than acetonitrile can be incorporated into the sixth coordination site. Reaction of [RuCl₂L₂] with PPh₃ in refluxing 1,2-dichloroethane gave [RuCl₂L₂(PPh₃)], **8**, as a

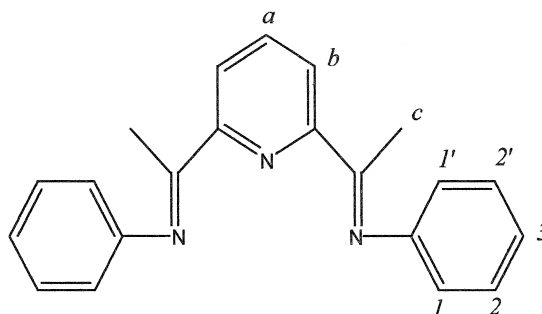
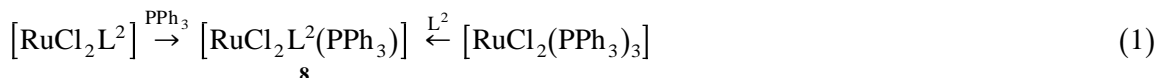


Fig. 1. Atom labeling scheme for ^1H NMR assignments.

red-brown crystalline solid. The same compound was also obtained from the reaction of L^2 with $[\text{RuCl}_2(\text{PPh}_3)_3]$ in refluxing toluene, Eq. (1). Thus, there is no problem accommodating ligands as bulky as PPh_3 in these complexes. However, here we do not wish to imply that PPh_3 is *trans* to the pyridine nitrogen; in fact NMR data would also be consistent with an axial PPh_3 .



Elemental analysis and NMR data are consistent with the proposed structure for **8**. In the ^1H NMR spectrum of **8** the methyl and the methoxy protons are observed as singlets at 2.32 and 3.85 ppm, respectively, whereas the pyridine protons are complex multiplets at 7.29–7.42 ppm. The $^{31}\text{P}\{\text{H}\}$ NMR spectrum showed a singlet at 32.9 ppm.

2.2. Catalytic epoxidation of cyclohexene

Metal complexes able to catalyze the selective oxidation of organic substrates under mild conditions are very attractive for many industrial processes [31]. In this context, the versatility of ruthenium(II) complexes via $\text{Ru}=\text{O}$ species has been explored [32–40]. An important feature of high-valent $\text{Ru}=\text{O}$ complexes is their capability to oxidize C–H and C=C bonds. A number of ruthenium complexes exhibit good selectivities for the conversion of norbornene, cyclooctene, and linear alkenes to their respective epoxides, but in the case of cyclohexene, allylic attack is normally dominant to yield 2-cyclohexene-1-ol, 2-cyclohexene-1-one, etc. [32–34]. However, the bisoxazoline complex, $[\text{RuCl}_2(\text{biox})_2]$, has very recently been reported as a stereospecific and regioselective epoxidation catalyst [38].

We have observed that some ruthenium(II) complexes of pydim, $[\text{RuCl}_2(\text{pydim})]$ and the acetonitrile adduct, $[\text{RuCl}_2(\text{pydim})(\text{NCCH}_3)]$, are effective catalysts for cyclohexene epoxidation by iodosobenzene (PhIO) in 1,2-dichloroethane. The results are presented in Table 4.

When a mixture of 0.01 mmol of $[\text{RuCl}_2\text{L}]$ or $[\text{RuCl}_2\text{L}(\text{NCMe})]$ and 0.5 mmol of PhIO was allowed to react at 22°C with a solution of cyclohexene (0.5 mmol) in DCE a slow reaction (ca. 4 turnover/h) ensued to produce cyclohexene oxide in a modest yield. In addition, minor amounts of byproducts were found, among which was 2-cyclohexene-1-one (< 5% of the products). The reactions were monitored by GC and products identified by comparison to authentic samples. The study showed that the ligands with one Me or one Bu^t substituent *ortho* to the imine nitrogens gave lower yields of epoxidation (entries 1 and 2). Whereas, Me, OMe or Bu^t substituents in the *p*-position of the phenyl ring do not inhibit the epoxidation and even enhance it (entries 3, 4 and 5). The

Table 2

Summary of crystallographic data, collection parameters and refinement parameters for compound **2**

Empirical formula	C ₂₇ H ₂₆ N ₄ Cl ₂ O ₂ Ru
Formula weight	586.48
Crystal dimensions (mm)	0.35 × 0.30 × 0.20
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	12.0587(5)
<i>b</i> (Å)	14.4898(6)
<i>c</i> (Å)	14.7997(7)
β (°)	92.896(1)
Cell volume (Å ³)	2575.64(19)
<i>Z</i>	4
<i>F</i> (000)	1188.70
<i>D</i> calc (Mg/m ³)	1.512
2 θ range (deg)	3.00 < 2 θ < 45.00
μ (mm ⁻¹)	0.85
Number of reflections measured	10538
Number of unique reflections	3357
Number of reflections with 1 net	2940
3.0 sigma (1 net)	
Merging <i>R</i> -value on intensities	0.060

2,6-dimethylaniline-derived ligand was found to be the best of the pydim ligands (entries 6 and 7). PPh₃ and MeCN complexes are generally less effective, (see entries 8 and 9), but in the case of the 2,6-*ortho*-dimethyl substituted system the acetonitrile complex gives higher yields of epoxide (entry 7). Under the same conditions isomeric complexes, i.e., **5** or **7**, are less effective than **6** (entries 7, 10 and 11). Since **5** and **6** are electronically very similar, steric factors seem to play an important role. Thus, an appropriate choice of substituents around the aryl rings may lead to a more favorable epoxidation catalyst. To our surprise, the Ru(II) complexes of related ligands (e.g., pybox or pybmbim) gave no epoxidation of cyclohexene (entries 12 and 13).

All catalytic reactions were run at room temperature (22°C); at higher temperature (65–70°C) the epoxide yield was lower (entry 14). It is worth noting that the mole ratio of PhIO:cyclohexene has a significant effect on the epoxide yield. Thus, the yield increased as the ratio increased from 1:1 to 2:1 (compare entries 15, 16 with 5, 7), but did not improve significantly upon further increase to 3:1. Increasing the substrate concentration exhibited the opposite effect (entry 17). This is in sharp contrast to that of [RuCl(diphos)₂]PF₆/PhIO system for which a reversible catalyst-substrate intermediate has been proposed [35–37].

We have observed that the amount of PhI released during the catalytic reaction does not reflect the amount of the oxygen transferred. Consequently, for epoxidation reactions by PhIO, an excess of oxidant is required [35–38]. It is found that even in the absence of cyclohexene, the Ru–pydim complexes react with PhIO to yield PhI and liberate significant amount of oxygen as PhIO becomes solubilized. The possible fate of the ‘lost oxygen’ has been discussed by Yang et al. [41] and they concluded that only a small part of the ‘lost oxygen’ could be attributed to solvent oxidation.

Replacement of PhIO by other oxidants such as H₂O₂, O₂, O₂/PhCHO or N-oxides and the influence of the solvent and additives were also studied. The use of oxidants H₂O₂, O₂ or O₂/PhCHO failed to give any reaction, whereas *N*-methylmorpholine *N*-oxide (MNO) and pyridine *N*-oxide were converted into their corresponding heterocycles (entries 18–22). The oxidation reactions were carried out in polar and non-polar solvents with [RuCl₂L³] as catalyst. The yield of

Table 3

Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for [RuCl₂L²(NCCH₃)], **2**

Bond	Length
Ru(1)–Cl(1)	2.392(3)
Ru(1)–Cl(2)	2.371(3)
Ru(1)–N(1)	2.093(9)
Ru(1)–N(4)	2.068(8)
Ru(1)–N(12)	1.906(7)
Ru(1)–N(15)	2.038(9)
N(1)–C(2)	1.121(15)
C(2)–C(3)	1.447(16)
N(4)–C(5)	1.313(12)
N(4)–C(16)	1.446(14)
C(5)–C(6)	1.503(15)
C(5)–C(7)	1.460(15)
C(7)–N(12)	1.376(13)
C(19)–O(22)	1.407(14)
Bond	Angle
Cl(1)–Ru(1)–Cl(2)	176.91(9)
Cl(1)–Ru(1)–N(1)	87.54(23)
Cl(1)–Ru(1)–N(4)	90.85(23)
Cl(1)–Ru(1)–N(12)	93.20(24)
Cl(1)–Ru(1)–N(15)	92.37(24)
Cl(2)–Ru(1)–N(1)	89.47(23)
Cl(2)–Ru(1)–N(4)	90.39(23)
Cl(2)–Ru(1)–N(12)	89.80(24)
Cl(2)–Ru(1)–N(15)	87.50(24)
N(1)–Ru(1)–N(4)	99.4(3)
N(1)–Ru(1)–N(12)	179.1(3)
N(1)–Ru(1)–N(15)	101.8(3)
N(4)–Ru(1)–N(12)	80.0(3)
N(4)–Ru(1)–N(15)	158.7(3)
N(12)–Ru(1)–N(15)	78.8(3)
Ru(1)–N(1)–C(2)	173.3(9)
N(1)–C(2)–C(3)	178.8(14)
Ru(1)–N(4)–C(5)	113.0(7)
Ru(1)–N(4)–C(16)	124.1(6)
C(5)–N(4)–C(16)	122.9(8)
N(4)–C(5)–C(6)	125.0(9)
N(4)–C(5)–C(7)	116.5(9)
C(6)–C(5)–C(7)	118.5(8)
C(5)–C(7)–C(8)	128.3(9)

epoxide decreases in the order ClCH₂CH₂Cl > CH₂Cl₂ > C₆H₅CH₃ (entries 5, 23, and 24). The reaction is inhibited by strongly coordinating solvents such as acetone or acetonitrile (entries 25 and 26). The catalytic activities of the acetonitrile adducts, i.e., [RuCl₂L(NCMe)], were less than corresponding [RuCl₂L] species (entries 5 and 8). However, [RuCl₂L⁶(NCMe)] is an exception (entry 7). Additives such as L³ or pyridine decreased the epoxidation yield (entries 27 and 28). In the presence of 0.02 mmol pydim (e.g., L³) or pyridine N-oxide which in situ is readily converted into pyridine itself, the epoxidation is almost completely inhibited. As mentioned above, an excess of cyclohexene also has a retarding effect. Tai et al. [42] have proposed that metal-catalyzed oxidation by PhIO proceeds via a M–O–I–Ph reactive intermediate. Our attempts to isolate or characterize the

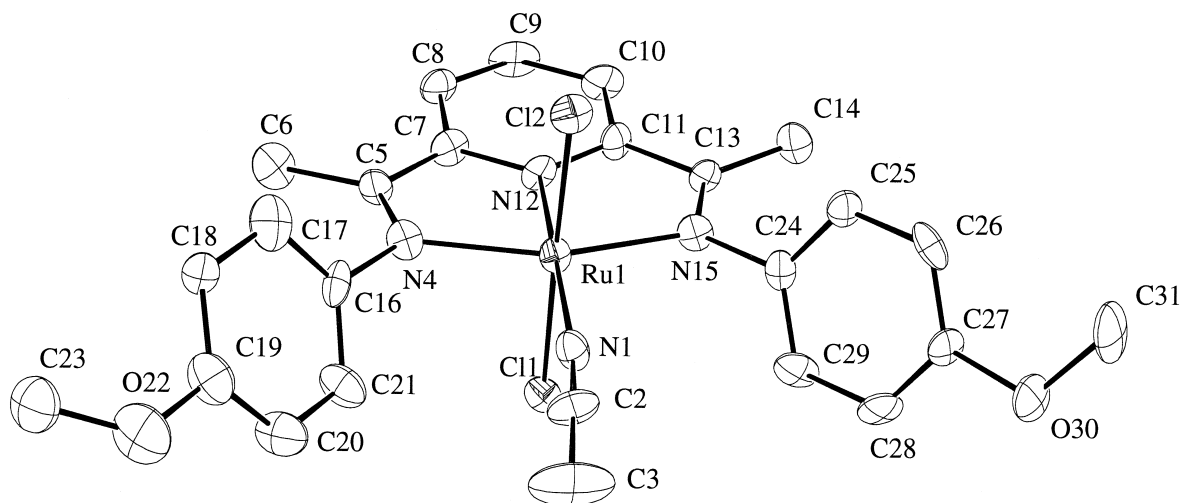


Fig. 2. ORTEP diagram of (acetonitrile)dichloro-[2,6-bis[1-(4-methoxyphenylimino)ethyl]pyridine]ruthenium(II), 2.

active catalytic species in solution were unsuccessful. Therefore, we cannot unambiguously identify the structure of the reactive complex that is responsible for the observed epoxidation reaction. Further investigations of the mechanistic details are needed and are in progress.

3. Experimental section

All manipulations were performed under argon using standard Schlenk techniques. ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra were obtained on a Varian Gemini 2000—300 MHz spectrometer operating at 300, 75.4, 121.5 and 282.3 MHz. Purity of the substrate and analysis of the products were determined on a Hewlett-Packard 5890A gas chromatograph using a Supelco Petrocol DH 50.2 capillary column (50 m, 0.20 mm i.d., 0.50 μm film thickness) and a flame ionization detector. Elemental analyses were performed by Atlantic Microlab.

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Johnson and Mathey), 2,6-diacetylpyridine and α -phellandrene (Fluka), and substituted anilines (Aldrich) were used as received. $[\text{RuCl}_2(p\text{-cymene})]_2$ [28] and $[\text{RuCl}_2(\text{PPh}_3)_3]$ [43] were synthesized according to published procedures. PhIO was prepared by hydrolysis of iodobenzene diacetate (Aldrich) and the samples were stored in a freezer [44].

3.1. Ligands (pydim)

The general conditions for the preparation of pydim ligands were as follows. 2,6-Diacetylpyridine (1.00 g, 6.14 mmol), the required aniline (15 mmol), a catalytic amount of glacial acetic acid (2–3 drops) and methanol (10 ml) were heated under reflux for 1–4 h. Upon cooling to room temperature yellow crystals were deposited. They were filtered off, washed with pentane (3×5 ml) and dried. In the case of L^6 and L^7 , longer refluxing periods (24 and 4 h, respectively) and a large excess of the aniline (20 mmol) were required for completion of the condensation. ^1H NMR data are presented in Table 1. The yields, melting points, microanalytical and ^{13}C NMR data are given below.

L^3 (1.80 g, 69%). Mp: 199–200°C. Anal. calcd. for $\text{C}_{29}\text{H}_{35}\text{N}_3$: C, 81.88; H, 8.24; N, 9.88. Found: C, 81.7; H, 8.3; N, 9.8. ^{13}C NMR: δ 167.2, 155.8, 148.3, 146.2, 138.8, 125.8, 122.2, 119.1, 34.3, 16.2.

Table 4

Effect of catalyst (0.01 mmol), solvent (5 ml), oxidant (0.5 mmol) and additives on the epoxidation of cyclohexene (0.5 mmol) at 22°C for 8 h^f

Entry	Metal complex	Solvent	Oxidant	Yield ^a	Ton ^b
1	[RuCl ₂ L ⁵]	DCE	PhIO	5	2.5
2	[RuCl ₂ L ⁴]	DCE	PhIO	9	4.5
3	[RuCl ₂ L ¹]	DCE	PhIO	26	13
4	[RuCl ₂ L ²]	DCE	PhIO	25	12.5
5	[RuCl ₂ L ³]	DCE	PhIO	27	13.5
6	[RuCl ₂ L ⁶]	DCE	PhIO	31	15.5
7	[RuCl ₂ L ⁶ (NCMe)]	DCE	PhIO	42	21
8	[RuCl ₂ L ² (PPh ₃)]	DCE	PhIO	10	5
9	[RuCl ₂ L ³ (NCMe)]	DCE	PhIO	10	5
10	[RuCl ₂ L ⁵ (NCMe)]	DCE	PhIO	13	6.5
11	[RuCl ₂ L ⁷ (NCMe)]	DCE	PhIO	18	9
12	[RuCl ₂ (Pybox)]	DCE	PhIO	< 1	–
13	[RuCl ₂ (Pybmbim)]	DCE	PhIO	< 1	–
14	[RuCl ₂ L ³]	DCE	PhIO	13 ^c	6.5
15	[RuCl ₂ L ³]	DCE	PhIO	37 ^d	18.5
16	[RuCl ₂ L ⁶ (NCMe)]	DCE	PhIO	65 ^d	32.5
17	[RuCl ₂ L ³]	DCE	PhIO	18 ^e	9
18	[RuCl ₂ L ³]	DCM	H ₂ O ₂	< 0.5	–
19	[RuCl ₂ L ³]	DCE	O ₂	< 0.5	–
20	[RuCl ₂ L ³]	DCE	O ₂ /PhCHO	< 0.5	–
21	[RuCl ₂ L ³]	DCE	MNO	< 0.5 ^f	–
22	[RuCl ₂ L ³]	DCE	PyNO	> 0.5 ^g	–
23	[RuCl ₂ L ³]	DCM	PhIO	18	9
24	[RuCl ₂ L ³]	PhMe	PhIO	5	2.5
25	[RuCl ₂ L ³]	Me ₂ CO	PhIO	< 1	–
26	[RuCl ₂ L ³]	MeCN	PhIO	< 1	–
27	[RuCl ₂ L ³]	DCE	PhIO	< 1 ^h	–
28	[RuCl ₂ L ³]	DCE	PhIO	4 ⁱ	2

[†]Abbreviations: DCE, 1,2-dichloroethane; DCM, dichloromethane; MNO, *N*-methymorpholine N-oxide; PhIO, iodosobenzene; Pybox, 2,6-bis(oxazolin-2-yl)pyridine; Pybmbim, 2,6-bis(*N*-methylbenzimidazol-2-yl)pyridine; PyNo, pridine N-oxide.

^aDetermined by GC, *n*-octane used as internal standard.

^bTON is amount (mmol) of epoxide formed per mmol of catalyst.

^cReaction carried out at 65–70°C.

^d1.0 mmol PhIO used.

^e2.0 mmol olefin used, yield based on PhIO.

^fN-oxide converted into *N*-methylmorpholine.

^gN-oxide converted into pyridine.

^h0.02 mmol L³ added.

ⁱ0.02 mmol pyridine N-oxide added.

L⁴ (1.54 g, 58%). Mp: 132–133°C. Anal. calcd. for C₂₉H₃₅N₃: C, 81.88; H, 8.24; N, 9.88. Found: C, 81.7; H, 8.3; N, 9.8. ¹³C NMR: δ 165.3, 155.6, 149.6, 139.7, 136.9, 126.5, 126.4, 123.8, 122.3, 119.8, 35.1, 29.6, 16.9.

L⁵ (1.85 g, 81%). Mp: 118–119°C. Anal. calcd. For C₂₅H₂₇N₃: C, 81.30; H, 7.32; N, 11.37. Found: C, 81.1; H, 7.4; N, 11.5. ¹³C NMR: δ 166.9, 155.5, 147.4, 136.7, 132.9, 131.1, 127.1, 126.9, 122.2, 118.1, 20.8, 17.7, 16.2.

L⁶ (1.69 g, 61%). Mp: 172–173°C. Anal. calcd. for C₂₅H₂₇N₃: C, 81.30; H, 7.32; N, 11.38. Found: C, 80.7; H, 7.5; N, 11.3. ¹³C NMR: δ 167.2, 155.2, 148.8, 136.9, 127.9, 125.4, 123.2, 122.3, 18.0, 16.5.

L⁷ (1.18 g, 52%). Mp: 127–129°C. Anal. calcd. for C₂₅H₂₇N₃: C, 81.30, H, 7.32; N, 11.38. Found: C, 80.5; H, 7.4; N, 11.3. ¹³C NMR: δ 167.0, 155.6, 151.3, 138.6, 136.8, 125.3, 125.2, 122.2, 116.9, 21.4, 16.2.

3.2. General procedure for the preparation of ruthenium complexes 1–7

[RuCl₂(*p*-cymene)]₂ (306 mg, 0.50 mmol) and 1.06 equivalent of the corresponding pydim(L) were dissolved in CH₂Cl₂ (10 ml) and the solution was heated under reflux for 10 h. The resulting deep purple solution was cooled to room temperature and was concentrated to ca. 5 ml in vacuo. The products were precipitated by addition of pentane (15 ml), filtered, washed with pentane (2 × 10 ml) and dried. However, *o*-substituted Schiff bases (L⁴–L⁶) were sluggish and gave incomplete substitution reactions with [RuCl₂(*p*-cymene)]₂ in CH₂Cl₂ or even in boiling ClCH₂CH₂Cl. Fortunately, however, boiling ethyl alcohol (10 ml) was found to induce complete displacement of *p*-cymene. After the reaction the solvent was removed to dryness in vacuo. The residue was dissolved in CH₂Cl₂ (5 ml) and was precipitated by addition of pentane (15 ml). The microcrystalline precipitates, containing one molecule of CH₂Cl₂ per molecule of the complex, were used as the epoxidation catalysts.

For full characterization, each complex can be converted into the hexacoordinated acetonitrile adducts by warming [RuCl₂L] in CH₃CN/ClCH₂CH₂Cl (0.5:5 ml) or in CH₃CN/CH₂Cl₂ and then adding pentane (10 ml). Here, a more direct method was employed, i.e., a solution of [RuCl₂(*p*-cymene)]₂ (0.50 mmol) and pydim (1.06 mmol) was refluxed in EtOH or CH₂Cl₂ (10 ml). After the reaction, the alcohol was replaced by CH₂Cl₂ or ClCH₂CH₂Cl (5 ml), and acetonitrile (0.5 ml). Pentane (10 ml) was then added to precipitate the complexes 1–7 which are generally solvated with CH₂Cl₂ or ClCH₂CH₂Cl. ¹H NMR data are given in Table 1 together with data for the corresponding ligands. The reported yields are based on the [RuCl₂(*p*-cymene)]₂ used.

1 (0.45 g, 82%). Mp: > 300°C. Anal. calcd. for C₂₅H₂₆N₄Cl₂Ru: C, 54.15; H, 4.69; N, 10.11. Found: C, 53.7; H, 4.7; N, 10.0. ¹³C NMR: δ 169.5, 162.8, 147.2, 135.7, 128.7, 127.1, 125.7, 121.1, 20.5, 17.0, 3.2.

2 (0.45 g, 80%). Mp: > 300°C. Anal. calcd. for C₂₅H₂₆N₄Cl₂O₂Ru: C, 51.19; H, 4.44; N, 9.56. Found: C, 49.7; H, 4.6; N, 9.2. ¹³C NMR: δ 169.7, 163.1, 158.0, 143.2, 127.4, 126.1, 123.7, 122.3, 113.5, 55.4, 17.3, 1.7.

3 (0.56 g, 76%). Mp: > 300°C. Anal. calcd. for C₃₁H₃₈N₄Cl₂Ru · ClCH₂CH₂Cl: C, 53.73; H, 5.70; N, 7.60. Found: C, 53.9; H, 5.7; N, 7.7. ¹³C NMR: δ 169.8, 163.2, 149.2, 147.5, 127.5, 125.9, 125.4, 122.5, 122.1, 44.0, 34.5, 31.2, 17.4, 3.5.

4 (0.31 g, 58%). Mp: > 300°C. Anal. calcd. for C₃₁H₃₈N₄Cl₂Ru: C, 58.30; H, 5.96; N, 8.78. Found: C, 57.1; H, 5.8; N, 8.5. ¹³C NMR: δ 173.7, 163.5, 148.9, 141.5, 128.8, 128.0, 126.6, 126.0, 125.7, 123.8, 36.3, 31.8, 19.8, 3.2.

5 (0.39 g, 60%). Mp: > 300°C. Anal. calcd. for C₂₇H₃₀N₄Cl₂Ru · CH₂Cl₂: C, 50.38; H, 4.80; N, 8.41. Found: C, 51.7; H, 4.9; N, 8.4. ¹³C NMR: δ 170.7, 162.8, 146.5, 135.3, 130.8, 129.2, 126.2, 126.1, 125.8, 122.7, 122.2, 20.4, 18.2, 17.0, 3.1.

6 (0.49 g, 74%) Mp: > 300°C. Anal. calcd. for C₂₇H₃₀N₄Cl₂Ru · CH₂Cl₂: C, 50.38; H, 4.80; N, 8.40. Found: C, 50.5; H, 4.9; N, 8.7. ¹³C NMR: δ 172.9, 162.9, 147.9, 131.8, 128.7, 128.4, 125.3, 123.7, 20.4, 17.9, 3.1.

7 (0.45 g, 68%) Mp: > 300°C. Anal. calcd. for C₂₇H₃₀N₄Cl₂Ru · CH₂Cl₂: C, 55.67; H, 5.15; N, 9.62. Found: C, 54.5 H, 5.1; N, 9.4. ¹³C NMR: δ 170.0, 163.4, 150.1, 138.4, 128.1, 128.0, 126.2, 122.6, 120.4, 120.3, 44.2, 21.4, 17.6, 3.5.

3.3. Synthesis of $[RuCl_2L^2(PPh_3)]$ (**8**)

Two different methods were used for the synthesis of **8**.

3.3.1. Method (i)

A solution of $[RuCl_2(p\text{-cymene})]$ (92 mg, 0.30 mmol) and L^2 (112 mg, 0.30 mmol) in $ClCH_2CH_2Cl$ (3 ml) was refluxed for 10 min. The resulting deep-purple solution was cooled to 25°C and PPh_3 (78 mg, 0.30 mmol) was added and the solution refluxed for a further 10 min. while the color turned into red-brown. The solution was cooled to 25°C, Et_2O (10 ml) was added to obtain a crystalline product which was filtered, washed with Et_2O (2×5 ml) and dried in vacuo. Yield: 0.22 g, 89%. Mp: > 300°C.

3.3.2. Method (ii)

A mixture of $[RuCl_2(PPh_3)_3]$ (0.32 g, 0.33 mmol) and L^2 (0.12 g, 0.35 mmol) in toluene (10 ml) was heated under reflux for 4 h. Volatiles were removed. The residue was dissolved in CH_2Cl_2 (5 ml) and then Et_2O (10 ml) was added to precipitate the product which was filtered and washed with hexane (2×10 ml) and dried. Yield: 0.24 g, 96%. This material was identical in every respect to the product obtained by method (i).

^{13}C NMR: δ 171.4, 163.0, 158.5, 141.1, 132.9, 132.3, 131.7, 129.0, 128.0, 127.2, 124.8, 112.4, 55.6, 18.2. ^{31}P NMR: δ 32.9 (s).

3.4. General procedure for reactions of cyclohexene with oxidants in the presence of metal catalysts

In a typical oxidation reaction, the catalysts (0.01 mmol) and the olefin was dissolved in 5 ml solvent. Co-oxidants (0.5 mmol, unless otherwise stated) were added all at once to the solution under argon with constant stirring. Aliquots were taken at timed intervals and analyzed by GLC; *n*-octane was used as internal standard.

3.5. X-ray structure determinations

An X-ray quality crystal of **2** was grown by diffusion of pentane into a $CH_3CN/ClCH_2CH_2Cl$ solution at 22°.

The intensity data were collected at $-100^\circ C$ on a Siemens SMART diffractometer, using the omega scan mode and graphite monochromated MoK_α radiation. The structure was solved using direct methods. The last least squares cycle, calculated with 60 atoms, 308 parameters and 2719 out of 3357 reflections resulted in a final $R = 0.076$, $R_w = 0.104$. Crystals diffracted very poorly so data was cut off at 45°. All computations were performed using the NRCVAX suite of programs.

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