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Ruthenium(II)–carbonyl complexes containing two *N*-monodentate 1,8-naphthyridine ligands: active catalysis in transfer hydrogenation reactions

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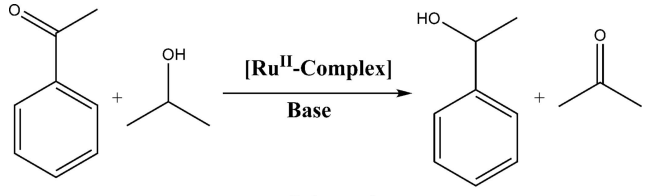
The reaction of 2-aminonicotinaldehyde with 2- or 4-methoxyacetophenone in basic media leads to the new ligands 2-(4-methoxyphenyl)-1,8-naphthyridine and 2-(2-methoxyphenyl)-1,8-naphthyridine, respectively, in high yield. The reaction of these naphthyridine derivatives with $[RuCl_2(CO)_2]_n$ leads to the respective complexes *cis*-dicarbonyldichloridobis[2-(4-methoxyphenyl)-1,8-naphthyridine-κN^8]ruthenium(II) and *cis*-dicarbonyldichloridobis[2-(2-methoxyphenyl)-1,8-naphthyridine-κN^8]ruthenium(II), both $[RuCl_2(C_{15}H_{12}N_2O)_2(CO)_2]$, in good yield. Both ruthenium(II) complexes display a slightly distorted octahedron with two *cis* carbonyl, two *cis* chloride and two *cis* naphthyridine ligands, the latter coordinated in a monodentate fashion through the N atom in the 8-position. Both complexes exhibit a moderate catalytic activity in the hydrogen-transfer reaction from propan-2-ol to acetophenone in the presence of a base, with 100% selectivity.

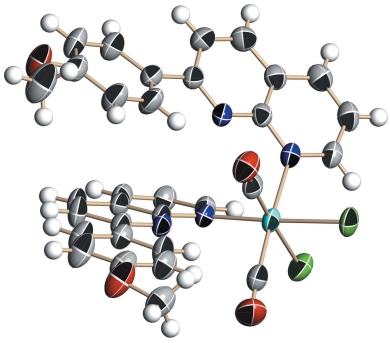
1. Introduction

The reduction of ketones or aldehydes is an important reaction in organic synthesis. One of the most commonly used methods to achieve this is a hydrogen-transfer reaction (HTR) (Scheme 1). It is a valuable atom-efficient reaction and, compared with conventional hydrogenation using molecular hydrogen, transfer hydrogenation offers a safer, more cost effective and simpler experimental procedure. A large number of alcohols and other reagents are available as a source of hydrogen and mild reaction conditions are used (Ozcan *et al.*, 2011).



Scheme 1

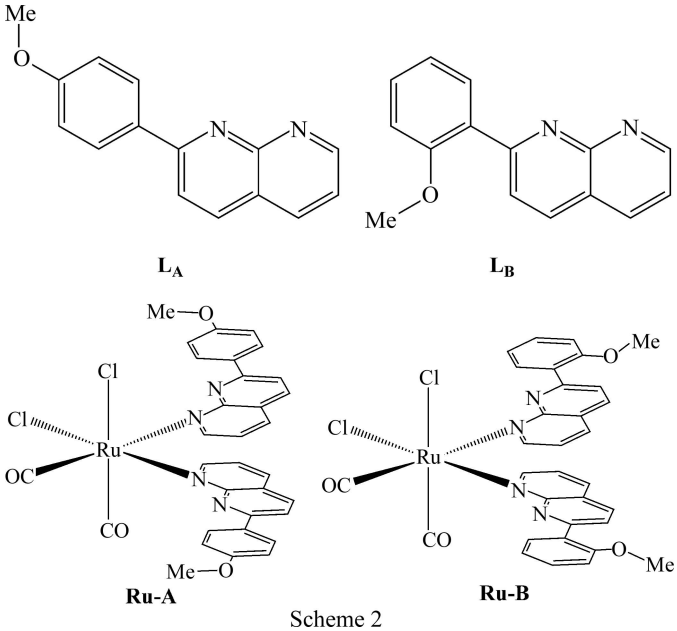
Transfer hydrogenation of ketones by propan-2-ol is convenient in large-scale synthesis, since there is no need to employ a high hydrogen pressure or to use hazardous reducing agents. Transition-metal complexes containing a coordinatively unsaturated metal centre and a Brönsted basic π-donor ligand have been reported to be active in homogeneous transfer hydrogenation.



Ruthenium complexes containing pyridine and phenanthroline ligands have been widely explored during the last two decades with regard to the hydrogen-transfer reaction (Moya *et al.*, 2012, Bhaskar *et al.*, 2016; Khusnutdinova & Milstein; 2015; Frank & Katritzky, 1976; Fujita *et al.*, 2014).

We have investigated the synthesis of ruthenium(II) complexes containing polypyridine ligands and their application as potential homogeneous catalysts. We found that these compounds are active in transfer hydrogenation. The active species has been described as being a ruthenium hydride complex containing 2,2-bipyridine, phenanthroline and 1,8-naphthyridine ligands (Aguirre *et al.*, 2001, 2003; Gajardo *et al.*, 2006; Oyama *et al.*, 2009; Moya *et al.*, 2012, 2013).

In the present article, we report the syntheses of two new ligands, namely 2-(4-methoxyphenyl)-1,8-naphthyridine, **L$_A$**, and 2-(2-methoxyphenyl)-1,8-naphthyridine, **L$_B$** (see Scheme 2), and their respective dichloridodicarbonylruthenium(II) complexes *cis*-dicarbonyldichloridobis[2-(4-methoxyphenyl)-1,8-naphthyridine-κN^8]ruthenium(II), [RuCl$_2$(**L$_A$**)$_2$(CO)$_2$] (**Ru-A**), and *cis*-dicarbonyldichloridobis[2-(2-methoxyphenyl)-1,8-naphthyridine-κN^8]ruthenium(II), [RuCl$_2$(**L$_B$**)$_2$(CO)$_2$] (**Ru-B**). The structures of the complexes and their activity in hydrogen transfer is discussed.



Scheme 2

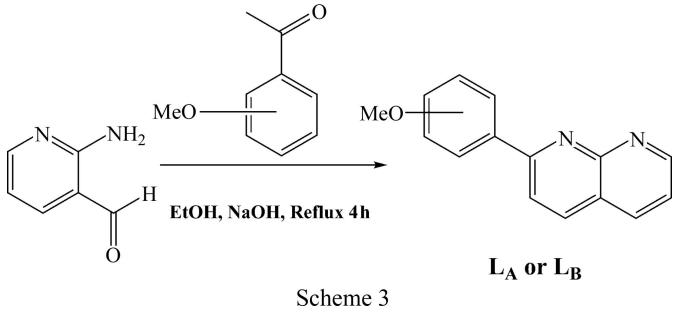
2. Experimental

2.1. Synthesis and crystallization

2.1.1. Synthesis of the ligands. A suspension of 2-aminonicotinaldehyde (500 mg, 4.09 mmol), 2- or 4-methoxy-substituted acetophenone (4.09 mmol) and NaOH (200 mg, 5 mmol) in EtOH (40 ml) was refluxed under argon for 4 h, as depicted in Scheme 3. After this period, the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 from an aqueous mixture and the organic layer was dried over magnesium sulfate. The product was purified by column chromatography on silica gel, eluting with CH_2Cl_2–EtOAc (6:1 *v*/*v*). After the solvent had been removed, the desired product was obtained as a white solid.

Analytical data for **L$_A$**: white solid; yield: 724 mg, 3.07 mmol, 75%; m.p. 430 K. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.10 (*dd*, H$_7$, J = 4.1, 1.9 Hz, 1H), 8.23 (*d*, Ph, J = 8.5 Hz, 2H), 8.15 (*d*, H$_4$, J = 8.4 Hz, 1H), 8.12 (*dd*, H$_5$, J = 8,1, 1.7 Hz, 1H), 7.90 (*d*, H$_3$, J = 8.0 Hz, 1H), 7.41 (*m*, H$_6$, 1H), 7.05 (*d*, Ph, J = 9.0, 2H), 3.90 (*s*, *p*-OMe, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 161.43 (C$_4$-Ph, 1C), 159.80 (C$_2$, 1C), 156.20 (C$_9$, 1C), 153.62 (C$_7$, 1C), 137.44 (C$_4$, 1C), 136.59 (C$_5$, 1C), 129.33 (C$_1$- Ph, 1C), 126.30 (C$_3$-Ph, C$_5$-Ph, 2C), 121.32 (C$_6$, C$_{10}$, 2C), 114.14 (C$_3$, 1C), 111.10 (C$_2$-Ph, C$_6$-Ph, 2C) 55.35 (*o*-OMe, 1C).

Analytical data for **L$_B$**: yellow solid; yield: 782 mg, 3.31 mmol, 81%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.01 (*dd*, H$_7$, J = 4.0, 2.0 Hz, 1H), 8.19 (*d*, H$_4$, J = 5.0 Hz, 1H), 8.17 (*d*, H$_5$, J = 4,2 Hz, 1H), 8.14 (*dd*, H$_3$, J = 4.5, 1.9 Hz, 1H), 8.10 (*dd*, Ph, J = 8.1, 1.3 Hz, 1H), 7.43 (*m*, H$_6$, 1H), 7.40 (*d*, Ph, J = 8.5 Hz, 1H), 7.13 (*dd*, Ph, J = 7.5, 0.9 Hz, 1H), 7.03 (*d*, Ph, J = 8.4 Hz, 1H), 3.89 (*s*, *o*-OMe, 3H).



Scheme 3

2.1.2. Synthesis of the complexes. Ligand **L$_A$** or **L$_B$** (1.316 mmol) and [RuCl$_2$(CO)$_2$]$_n$ (0.658 mmol) were mixed in ethanol–H_2O (9:1 *v*/*v*, 50 ml). The mixture was refluxed for 24 h under a nitrogen atmosphere. The precipitate was separated by filtration and the solid was washed with ethanol, acetone, chloroform and diethyl ether. X-ray diffraction quality crystals were grown from an ethanol–water (10:1 *v*/*v*) mixture.

Analytical data for **Ru-A**: yield 68%; m.p. 610 K. ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.54 (*dd*, H$_7$, J = 5.5, 2.2 Hz, 1H), 9.03 (*dd*, H$_{7'}$, J = 5.7, 1.8 Hz, 1H), 8.93 (*m*, H$_5$, Ph, 3H), 8.71 (*d*, H$_4$, J = 8.8 Hz, 1H), 8.68 (*d*, H$_{4'}$, J = 8.6 Hz, 1H), 8.59 (*d*, H$_{3'}$, J = 8.6 Hz, 1H), 8.42 (*dd*, H$_{5'}$, J = 8.1, 1.8 Hz, 1H), 8.21 (*d*, H$_3$, J = 8.8 Hz, 1H), 8.1 (*dd*, H$_6$, J = 8.2, 5.5 Hz, 1H), 7.50 (*m*, Ph′, Ph, 4H), 7.21 (*dd*, H$_{6'}$, J = 8.1, 5.7 Hz, 1H), 6.58 (*m*, Ph′, 2H), 4.14 (*s*, OMe, 3H), 3.91 (*s*, OMe, 3H). IR (KBr, cm^{-1}) *M*—CO 2050.0, 1988.2. Analysis calculated (%) for $C_{32}H_{24}Cl_2N_4O_4Ru$: C 54.86, H 3.45, N 8.00; found: C 54.09, H 3.95, N 7.98.

Analytical data for **Ru-B**: yield 50%; m.p. 560 K. ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.54 (*dd*, H$_7$, J = 5.5, 2.0 Hz, 1H), 9.05 (*dd*, H$_{7'}$, J = 5.5, 1,8 Hz, 1H), 8.93 (*m*, H$_5$, Ph, 3H), 8.68 (*d*, H$_{4'}$, J = 8.6 Hz, 1H), 8.71 (*d*, H$_4$, J = 8.8 Hz, 1H), 8.59 (*d*, H$_{3'}$, J = 8.6 Hz, 1H), 8.42 (*dd*, H$_{5'}$, J = 8.1, 1.8 Hz, 1H), 8.21 (*d*, H$_3$, J = 8.8 Hz, 1H), 8.10 (*dd*, H$_6$, J = 8.2, 5.5 Hz, 1H), 7.50 (*m*, Ph, Ph′, 4H), 7.21 (*dd*, H$_{6'}$, J = 8.1, 5.7 Hz, 1H), 7.03 (*m*, Ph′, 2H), 4.14 (*s*, *o*-OMe, 3H), 3.91 (*s*, *o*-OMe, 3H). IR (KBr, cm^{-1}) *M*—CO;

Table 1
Experimental details.

	Ru-A	**Ru-B**
Crystal data		
Chemical formula	$[RuCl_2(C_{15}H_{12}N_2O)_2(CO)_2]$	$[RuCl_2(C_{15}H_{12}N_2O)_2(CO)_2]$
M_r	700.52	700.52
Crystal system, space group	Triclinic, $P\overline{1}$	Monoclinic, $C2/c$
Temperature (K)	296	296
a, b, c (Å)	10.8018 (15), 11.6708 (16), 14.248 (2)	19.106 (3), 12.1967 (16), 29.420 (4)
α, β, γ (°)	93.707 (2), 105.555 (2), 116.417 (2)	90, 94.918 (2), 90
V (Å^3)	1514.1 (4)	6830.5 (17)
Z	2	8
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.74	0.66
Crystal size (mm)	0.27 × 0.26 × 0.05	0.27 × 0.26 × 0.05
Data collection		
Diffractometer	Bruker SMART CCD area detector	Bruker SMART CCD area detector
Absorption correction	Empirical (using intensity measurements) (*SADABS*; Bruker, 2012)	Empirical (using intensity measurements) (*SADABS*; Bruker, 2012)
T_{min}, T_{max}	0.819, 0.964	0.819, 0.964
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11949, 5886, 4861	26258, 6683, 4821
R_{int}	0.021	0.047
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.617	0.617
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.093, 1.04	0.042, 0.103, 0.98
No. of reflections	5886	6683
No. of parameters	390	391
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.76, −0.22	0.59, −0.25

Computer programs: *SMART* (Bruker, 2012), *SAINT* (Bruker, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *SHELXTL* (Bruker, 2012) and *publCIF* (Westrip, 2010).

2056.0, 1989.0. Analysis calculated (%) for $C_{32}H_{24}Cl_2N_4O_4Ru$: C 54.86, H 3.45, N 8.00%; found: C 54.04, H 3.91, N 7.89.

2.2. Catalysis assays

In a glass reactor fitted with a condenser, NaOH (0.5 mmol) was added to propan-2-ol (5 ml) and stirred for 1 h at 353 K under nitrogen. Next, the ruthenium complex (0.0125 mmol), propan-2-ol (4 ml) and a solution (1 ml) of *p*-cymene (1.92 mmol) were added to the corresponding substrate (25.6 mmol) dissolved in propan-2-ol, making a total volume of 10 ml. The identities of the reaction components were determined by gas chromatography by comparison with commercial samples.

2.3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The H-atom positions were calculated after each cycle of refinement using a riding model, with C—H = 0.93 and 0.97 Å for aromatic and aliphatic H atoms, respectively, and U_{iso}(H) = 1.2U_{eq}(parent). An ethanol solvent molecule, as suggested by ^{1}H NMR analysis, was found to be strongly disordered during the final stages of the refinement of **Ru-B**. Despite our efforts, no meaningful model was achieved. At this point, we choose to use SQUEEZE, a well-documented method (van der Sluis & Spek, 1990; Spek, 2015) for the modelling of unresolved electron density, to consider the effect of the disordered solvent. A total of 57 electrons per hole suggest, in addition to the experimental conditions, an ethanol molecule per molecule of complex.

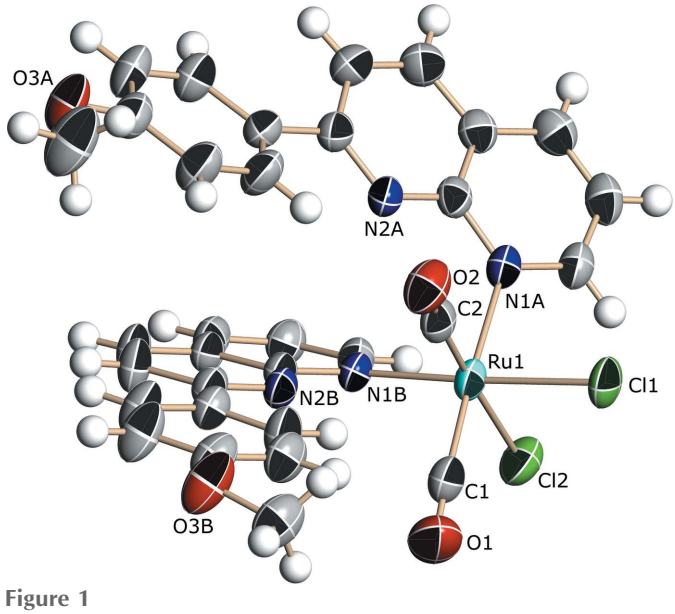


Figure 1
The molecular structure of complex **Ru-A**, showing a partial atom-numbering scheme. The atoms are shown as displacement ellipsoids at the 50% probability level, except for the H atoms, which are shown as spheres of arbitrary radii.

Table 2
Selected geometric parameters (Å, °) for **Ru-A**.

Ru1—C2	1.867 (3)	Ru1—N1*A*	2.175 (2)
Ru1—C1	1.879 (4)	Ru1—Cl1	2.4008 (8)
Ru1—N1*B*	2.116 (2)	Ru1—Cl2	2.4389 (9)
C2—Ru1—C1	90.63 (14)	N1*B*—Ru1—Cl1	175.75 (6)
C2—Ru1—N1*B*	95.79 (10)	N1*A*—Ru1—Cl1	89.23 (6)
C1—Ru1—N1*B*	94.98 (11)	C2—Ru1—Cl2	175.65 (8)
C2—Ru1—N1*A*	91.44 (11)	C1—Ru1—Cl2	87.83 (10)
C1—Ru1—N1*A*	177.08 (11)	N1*B*—Ru1—Cl2	88.40 (6)
N1*B*—Ru1—N1*A*	86.86 (8)	N1*A*—Ru1—Cl2	89.96 (6)
C2—Ru1—Cl1	85.94 (9)	Cl1—Ru1—Cl2	89.96 (3)
C1—Ru1—Cl1	88.88 (9)		
C10*A*—C11*A*—C12*A*—N2*A*	22.8 (4)		
C10*B*—C11*B*—C12*B*—N2*B*	−3.1 (4)		
C6*A*—C11*A*—C12*A*—N2*A*	−161.9 (3)		
C6*B*—C11*B*—C12*B*—N2*B*	−179.8 (3)		
C10*A*—C11*A*—C12*A*—C5*A*	−154.4 (3)		
C10*B*—C11*B*—C12*B*—C5*B*	175.9 (3)		
C6*A*—C11*A*—C12*A*—C5*A*	20.9 (4)		
C6*B*—C11*B*—C12*B*—C5*B*	−0.8 (5)		

Table 3
Selected geometric parameters (Å, °) for **Ru-B**.

Ru1—C1	1.861 (4)	Ru1—N1*A*	2.188 (3)
Ru1—C2	1.867 (4)	Ru1—Cl1	2.3974 (9)
Ru1—N1*B*	2.117 (2)	Ru1—Cl2	2.4400 (9)
C1—Ru1—C2	88.89 (14)	N1*B*—Ru1—Cl1	177.34 (7)
C1—Ru1—N1*B*	95.56 (12)	N1*A*—Ru1—Cl1	87.55 (7)
C2—Ru1—N1*B*	92.86 (11)	C1—Ru1—Cl2	88.59 (11)
C1—Ru1—N1*A*	173.79 (12)	C2—Ru1—Cl2	177.36 (9)
C2—Ru1—N1*A*	93.70 (11)	N1*B*—Ru1—Cl2	88.16 (7)
N1*B*—Ru1—N1*A*	89.95 (9)	N1*A*—Ru1—Cl2	88.74 (7)
C1—Ru1—Cl1	86.89 (11)	Cl1—Ru1—Cl2	90.88 (3)
C2—Ru1—Cl1	88.22 (9)		
C10*A*—C11*A*—C12*A*—N2*A*	42.6 (4)		
C10*B*—C11*B*—C12*B*—N2*B*	−45.4 (5)		
C6*A*—C11*A*—C12*A*—N2*A*	−134.1 (3)		
C6*B*—C11*B*—C12*B*—N2*B*	137.1 (4)		
C10*A*—C11*A*—C12*A*—C5*A*	−136.7 (4)		
C10*B*—C11*B*—C12*B*—C5*B*	128.8 (4)		
C6*A*—C11*A*—C12*A*—C5*A*	46.5 (5)		
C6*B*—C11*B*—C12*B*—C5*B*	−48.6 (5)		

3. Results and discussion

Two ruthenium(II) complexes with different substituted naphthyridine ligands have been prepared and characterized. The ligands $\mathbf{L_A}$ and $\mathbf{L_B}$ were synthesized from 2-aminonicotinaldehyde and the corresponding substituted acetophenone. The structures of complexes *cis*-[$RuCl_2(\mathbf{L_A})_2(CO)_2$] (**Ru-A**) and *cis*-[$RuCl_2(\mathbf{L_B})_2(CO)_2$] (**Ru-B**) were confirmed by X-ray crystallographic studies (Figs. 1 and 2). Tables 2 and 3 present selected bond lengths, angles and torsion angles for complexes **Ru-A** and **Ru-B**, respectively. To the best of our knowledge, previously described examples of the structures of dichloridodicarbonylruthenium(II)–naphthyridine complexes are scarce (Zúñiga *et al.*, 2011; Oyama & Hamada, 2008; Oyama *et al.*, 2017). The two title complexes have a slightly distorted octahedral geometry around the Ru^{II} centre, with the two naphthyridine ligands in *cis* positions with respect to each other; one is *trans* to a chloride ligand and the second is *trans* to a carbonyl ligand. The high steric hindrance of phenyl-substituted naphthyridine ligands does not preclude a *cis* configuration. As expected from the presence of a methoxy substituent at the 2-position of the phenyl group in **Ru-B**, this ring is not coplanar with the naphthyridine bicycle. This is reflected by the dihedral angles between the least-squares planes, defined by the naphthyridine bicycle and the phenyl group, of 46.63 (8) and 48.7 (1)° for both ligands. In contrast, for **Ru-A**, where the methoxy group occupies the 4-position, the corresponding values are much less at 6.6 (1) and 26.9 (1)°.

The syntheses of ruthenium compounds containing 1,8-naphthyridine derivatives have been reported by other authors, where the ligand acts as a bridging, a monodentate or a bidentate ligand (Majumdar *et al.*, 2010; Sinha *et al.*, 2013; Cohen *et al.*, 2010; Oyama *et al.*, 2011). The compounds reported here were prepared using a $[RuCl_2(CO)_2]_n$ precursor producing a mononuclear compound with the 1,8-naphthyridine ligands coordinated in a monodentate fashion. During the formation of the mononuclear complexes, 1,8-naphthyridine tends to act as either a monodentate or a bidentate ligand. However, chelation is generally disfavoured, due to the small bite angle of the resulting four-membered chelate ring (Tomon *et al.*, 2001). In the context of the bidentate coordination system, the 1,8-naphthyridine-containing compounds 2-(pyridin-2-yl)-1,8-naphthyridine and 3-(pyridin-2-yl)-4-azaacridine are multifunctional ligands that act as bidentate polypyridyl ligands. For example, ruthenium complexes containing bidentate 1,8-naphthyridine-type ligands have been reported for 2-(pyridin-2-yl)-1,8-naphthyridine, where the pyridine group increases the bite angle, thus allowing the κ^2-chelating mode (Cohen *et al.*, 2010).

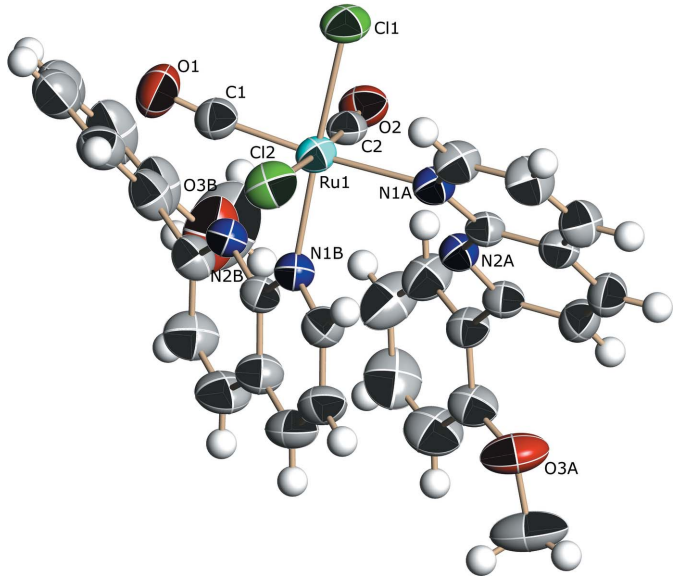
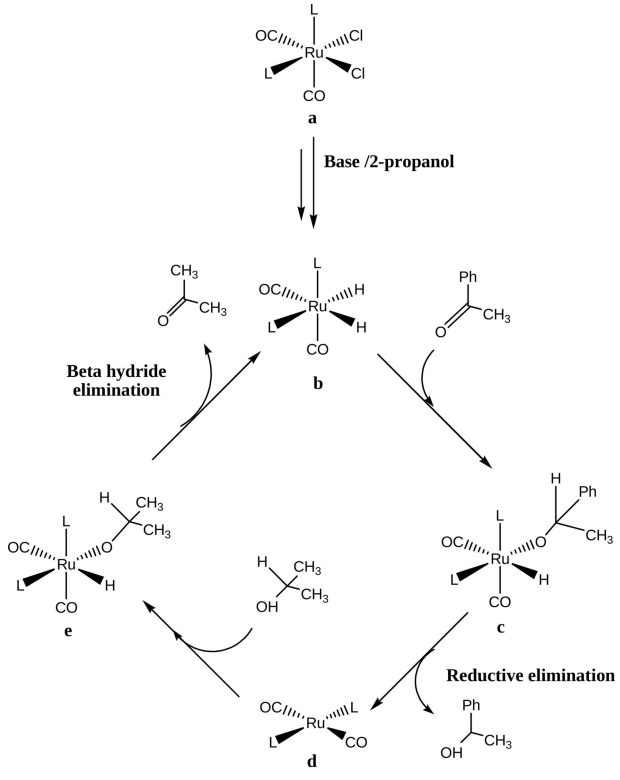


Figure 2
The molecular structure of complex **Ru-B**, showing a partial atom-numbering scheme. The atoms are shown as displacement ellipsoids at the 50% probability level, except for the H atoms, which are shown as spheres of arbitrary radii.

The catalytic activity in the transfer hydrogenation of acetophenone was shown by the ruthenium(II) complexes **Ru-A** and **Ru-B** in the presence of NaOH. In both cases, only one product, namely 1-phenylethanol, is obtained with 100% selectivity. Complex **Ru-A** produced a 95% (TOF = 190 h^{-1}) conversion after 1 h of reaction and complex **Ru-B** a 70% (140 h^{-1}) conversion after 1 h of reaction. The catalytic activities were studied using two substrate–catalyst ratios, *i.e.* 200:1 and 1000:1. When the concentration of substrate was increased, the conversion was 45% (TOF = 450 h^{-1}) for **Ru-A** and 35% (TOF = 350 h^{-1}) for **Ru-B** after 1 h of reaction; however, after 6 h of reaction, both catalysts showed 100% conversion. Both complexes exhibit a moderate catalytic activity in the transfer hydrogenation of acetophenone in the presence of a base. It is noteworthy that these complexes exhibit a 100% selectivity, the corresponding alcohol being formed, and a low load of the base (NaOH) is required to achieve the observed activities.



Scheme 4

The mechanism of the hydrogen-transfer reaction has been reported by several authors. Van Leeuwen (2004) reported a detailed mechanism for this reaction. As shown in Scheme 4, in the first stage, the dichloro precursor is converted into the metal dihydride complex **b**. Subsequent addition of the ketone then gives rise to the formation of the [Ru]–OC(CH_3)-(H)(Ph) species **c**. This latter undergoes reductive elimination to form the tetracoordinated metal complex **d**, together with a molecule of the hydrogenated product which leaves the cycle. This tetracoordinated intermediate then reacts with propan-2-ol to generate the metal hydride complex **e**. Finally, **e** experiences β-elimination, producing acetone and regenerating the dihydride hexacoordinated complex (*i.e.* **b**), thus closing the catalytic cycle. The key step in the hydrogen-transfer reaction mechanism is the substrate approach to the ruthenium hydride active catalyst. Our group has previously studied the mechanism for transfer hydrogenation using ruthenium(II) compounds containing pincer phosphorus–nitrogen ligands, where the ruthenium hydride (Ru–H) intermediate was detected by proton nuclear magnetic resonance (^{1}H NMR) during the catalytic reaction. The broad signal detected at −14.46 ppm (Moya *et al.*, 2017) was attributed to very reactive ruthenium hydride species, which reacts in the presence of any substrate or even solvent. The crystal structures of both complexes display *cis*-Cl and monodentate 1,8-naphthyridine. This would avoid obstacles for the substrate approaching to the complex during the catalytic cycle. This consequently suggests that both steps of the mechanism would take place easily for **Ru-A** and **Ru-B**, explaining the observed high activities.

Funding information

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References

Aguirre, P., López, R., Villagra, D., Azócar-Gúzman, I., Pardey, A. J. & Moya, S. A. (2003). *Appl. Organomet. Chem.* **17**, 36–41.
Aguirre, P., Sariego, R. & Moya, S. A. (2001). *J. Coord. Chem.* **54**, 401–413.
Bhaskar, P., Kaushik, C. & Sabuj, K. (2016). *Dalton Trans.* **45**, 11162–11171.
Bruker (2012). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cohen, B. W., Polyansky, D. E., Zong, R., Zhou, H., Ouk, T., Cabelli, D. E., Thummel, R. P. & Fujita, E. (2010). *Inorg. Chem.* **49**, 8034–8044.
Frank, J. & Katritzky, A. R. (1976). *J. Chem. Soc. Perkin Trans. 2*, pp. 1428–1431.
Fujita, K.-I., Tanaka, Y., Kobayashi, M. & Yamaguchi, R. (2014). *J. Am. Chem. Soc.* **136**, 4829–4832.
Gajardo, J., Araya, J. C., Moya, S. A., Pardey, A. J., Guerchais, V., Le Bozec, H. & Aguirre, P. (2006). *Appl. Organomet. Chem.* **20**, 272–276.
Khusnutdinova, J. R. & Milstein, D. (2015). *Angew. Chem. Int. Ed.* **54**, 12236–12273.
Majumdar, M., Sinha, A., Ghatak, T., Patra, S. K., Sadhukhan, N., Rahaman, S. M. W. & Bera, J. K. (2010). *Chem. Eur. J.* **16**, 2574–2585.
Moya, S. A., Araya, J. C., Gajardo, J., Guerchais, V., Le Bozec, H., Toupet, L. & Aguirre, P. (2013). *Inorg. Chem. Commun.* **27**, 108–110.
Moya, S. A., Negrete-Vergara, C., Brown, K., Artigas, V., Fuentealba, M., Guerchais, V. & Aguirre, P. (2017). *Catal. Commun.* **99**, 150–153.
Moya, S. A., Vidal, M., Brown, K., Negrete-Vergara, C., Abarca, G. & Aguirre, P. (2012). *Inorg. Chem. Commun.* **22**, 146–148.
Oyama, D., Asuma, A., Hamada, T. & Takase, T. (2009). *Inorg. Chim. Acta*, **362**, 2581–2588.
Oyama, D. & Hamada, T. (2008). *Acta Cryst.* E**64**, m442–m443.
Oyama, D., Hamada, T. & Takase, T. (2011). *J. Organomet. Chem.* **696**, 2263–2268.
Oyama, D., Yamanaka, T., Abe, R. & Takase, T. (2017). *J. Organomet. Chem.* **830**, 167–174.

Ozcan, E. O., Mercan, D., Gurbuz, N., Cetinkaya, E., Cetinkaya, B. & Ozdemir, I. (2011). *Turk. J. Chem.* **35**, 699–709.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Sinha, A., Majumdar, M., Sarkar, M., Ghatak, T. & Bera, J. K. (2013). *Organometallics*, **32**, 340–349.
Sluis, P. van der & Spek, A. L. (1990). *Acta Cryst.* A**46**, 194–201.
Spek, A. L. (2015). *Acta Cryst.* C**71**, 9–18.
Tomon, T., Oyama, D., Wada, T., Shiren, K. & Tanaka, K. (2001). *Chem. Commun.* pp. 1100–1101.
Van Leeuwen, P. W. N. M. (2004). *Homogeneous Catalysis Understanding the Art*, pp. 75–100 Dordrecht: Kluwer Academic.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Zúñiga, C., Moya, S. A., Fuentealba, M., Aranda, B. & Aguirre, P. (2011). *Inorg. Chem. Commun.* **14**, 964–967.

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Ruthenium(II)–carbonyl complexes containing two *N*-monodentate 1,8-naphthyridine ligands: active catalysis in transfer hydrogenation reactions

Juana Guajardo, Andrés Ibañez, Veronique Guerchais, Andrés Vega, Sergio Moya and Pedro Aguirre

Computing details

For both structures, data collection: *SMART* (Bruker, 2012); cell refinement: *SMART* (Bruker, 2012); data reduction: *SAINT* (Bruker, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Bruker, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

cis-Dicarbonyldichloridobis[2-(4-methoxyphenyl)-1,8-naphthyridine-κN^8]ruthenium(II) (Ru_A)

Crystal data

$[RuCl_2(C_{15}H_{12}N_2O)_2(CO)_2]$
M_r = 700.52
Triclinic, $P\overline{1}$
a = 10.8018 (15) Å
b = 11.6708 (16) Å
c = 14.248 (2) Å
α = 93.707 (2)°
β = 105.555 (2)°
γ = 116.417 (2)°
V = 1514.1 (4) Å^3
Z = 2
$F(000)$ = 708
D_x = 1.537 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 999 reflections
θ = 4.5–46.9°
μ = 0.74 mm^{-1}
T = 296 K
Plate, yellow
0.27 × 0.26 × 0.05 mm

Data collection

Bruker SMART CCD area detector diffractometer
Radiation source: fine focus sealed tube
phi and ω scans
Absorption correction: empirical (using intensity measurements) (SADABS; Bruker, 2012)
T_{min} = 0.819, T_{max} = 0.964
11949 measured reflections
5886 independent reflections
4861 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 26.0°, θ_{min} = 2.0°
h = −13→13
k = −14→14
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.093
S = 1.04
5886 reflections
390 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 0.1027P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.76 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)
6.9012 (0.0050) x - 10.8797 (0.0039) y + 3.1820 (0.0121) z = 1.3347 (0.0070)
* 0.0561 (0.0020) N1A * 0.0169 (0.0024) C1A * -0.0659 (0.0025) C2A * -0.0310 (0.0025) C3A * 0.0284 (0.0026) C14A * 0.0588 (0.0027) C4A * 0.0202 (0.0026) C5A * -0.0911 (0.0021) C12A * 0.0077 (0.0024) C13A
Rms deviation of fitted atoms = 0.0492
- 5.2857 (0.0138) x + 11.5034 (0.0032) y + 1.4914 (0.0197) z = 2.0137 (0.0126)
Angle to previous plane (with approximate esd) = 26.938 (0.100)
* 0.0042 (0.0023) C11A * -0.0001 (0.0024) C6A * -0.0021 (0.0026) C7A * 0.0003 (0.0025) C8A * 0.0039 (0.0026) C9A * -0.0063 (0.0026) C10A
Rms deviation of fitted atoms = 0.0036
- 0.5195 (0.0100) x + 10.0547 (0.0055) y + 2.0390 (0.0083) z = 1.5842 (0.0058)
Angle to previous plane (with approximate esd) = 28.060 (0.083)
* 0.0309 (0.0019) N1B * -0.0011 (0.0023) C1B * -0.0301 (0.0024) C2B * -0.0054 (0.0024) C3B * 0.0129 (0.0026) C14B * 0.0190 (0.0026) C4B * 0.0103 (0.0026) C5B * -0.0404 (0.0021) C12B * 0.0039 (0.0024) C13B
Rms deviation of fitted atoms = 0.0215
- 1.4570 (0.0156) x + 10.6670 (0.0066) y + 1.3367 (0.0212) z = 1.1428 (0.0074)
Angle to previous plane (with approximate esd) = 6.588 (0.131)
* -0.0003 (0.0023) C11B * 0.0020 (0.0026) C6B * -0.0024 (0.0027) C7B * 0.0010 (0.0026) C8B * 0.0008 (0.0025) C9B * -0.0011 (0.0024) C10B
Rms deviation of fitted atoms = 0.0015

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ru1	0.34638 (2)	0.15266 (2)	0.27576 (2)	0.04391 (10)
C1	0.2245 (3)	0.0235 (3)	0.1584 (3)	0.0568 (8)
C2	0.3888 (3)	0.2831 (3)	0.2017 (2)	0.0483 (7)
Cl1	0.14218 (8)	0.18405 (9)	0.27848 (6)	0.0595 (2)
Cl2	0.27212 (9)	−0.01997 (8)	0.36903 (7)	0.0635 (2)
O1	0.1472 (3)	−0.0529 (3)	0.0876 (2)	0.0893 (9)
O2	0.3996 (2)	0.3603 (2)	0.15678 (18)	0.0679 (6)
C1A	0.4212 (3)	0.2857 (3)	0.4881 (2)	0.0512 (7)
H1A	0.3261	0.2189	0.4754	0.061*
C2A	0.4950 (4)	0.3676 (3)	0.5821 (2)	0.0562 (8)
H2A	0.4471	0.3582	0.6287	0.067*
C3A	0.6368 (4)	0.4614 (3)	0.6060 (2)	0.0577 (8)
H3A	0.6888	0.5143	0.6696	0.069*
C4A	0.8492 (4)	0.5708 (3)	0.5479 (2)	0.0593 (8)
H4A	0.9090	0.6229	0.6111	0.071*
C5A	0.9019 (3)	0.5854 (3)	0.4713 (2)	0.0579 (8)
H5A	0.9991	0.6459	0.4818	0.069*
C6A	1.0098 (3)	0.6003 (3)	0.2985 (3)	0.0613 (9)
H6A	1.0797	0.6242	0.3612	0.074*
C7A	1.0536 (4)	0.6309 (4)	0.2168 (3)	0.0673 (10)
H7A	1.1531	0.6752	0.2252	0.081*
C8A	0.9530 (4)	0.5969 (3)	0.1236 (3)	0.0588 (8)

C9A	0.8047 (4)	0.5308 (3)	0.1107 (3)	0.0676 (10)
H9A	0.7351	0.5078	0.0480	0.081*
C10A	0.7622 (3)	0.4997 (3)	0.1929 (2)	0.0637 (9)
H10A	0.6625	0.4538	0.1837	0.076*
C11A	0.8598 (3)	0.5332 (3)	0.2876 (2)	0.0493 (7)
C12A	0.8088 (3)	0.5083 (3)	0.3745 (2)	0.0471 (7)
C13A	0.6209 (3)	0.3978 (3)	0.4352 (2)	0.0429 (6)
C14A	0.7029 (3)	0.4762 (3)	0.5319 (2)	0.0482 (7)
C15A	0.9070 (4)	0.6131 (5)	−0.0467 (3)	0.0978 (15)
H15A	0.8399	0.5210	−0.0699	0.147*
H15B	0.9588	0.6439	−0.0928	0.147*
H15C	0.8535	0.6593	−0.0419	0.147*
C1B	0.6010 (3)	0.1132 (3)	0.3711 (2)	0.0483 (7)
H1B	0.5567	0.1007	0.4200	0.058*
C2B	0.7346 (3)	0.1129 (3)	0.3928 (2)	0.0500 (7)
H2B	0.7770	0.0991	0.4540	0.060*
C3B	0.8014 (3)	0.1330 (3)	0.3224 (2)	0.0487 (7)
H3B	0.8917	0.1355	0.3356	0.058*
C4B	0.7922 (3)	0.1695 (3)	0.1523 (2)	0.0558 (8)
H4B	0.8826	0.1733	0.1613	0.067*
C5B	0.7186 (3)	0.1826 (3)	0.0649 (2)	0.0570 (8)
H5B	0.7590	0.1976	0.0140	0.068*
C6B	0.5443 (3)	0.1976 (3)	−0.1269 (2)	0.0636 (9)
H6B	0.6381	0.2097	−0.1183	0.076*
C7B	0.4603 (4)	0.1972 (4)	−0.2189 (3)	0.0713 (10)
H7B	0.4975	0.2084	−0.2714	0.086*
C8B	0.3209 (3)	0.1803 (3)	−0.2333 (2)	0.0584 (8)
C9B	0.2666 (3)	0.1631 (3)	−0.1558 (2)	0.0611 (9)
H9B	0.1730	0.1516	−0.1647	0.073*
C10B	0.3521 (3)	0.1632 (3)	−0.0643 (2)	0.0591 (8)
H10B	0.3141	0.1513	−0.0122	0.071*
C11B	0.4925 (3)	0.1803 (3)	−0.0470 (2)	0.0479 (7)
C12B	0.5787 (3)	0.1732 (3)	0.0506 (2)	0.0455 (7)
C13B	0.5956 (3)	0.1458 (3)	0.2115 (2)	0.0399 (6)
C14B	0.7333 (3)	0.1501 (3)	0.2300 (2)	0.0439 (7)
C15B	0.0925 (4)	0.1389 (4)	−0.3513 (3)	0.0735 (10)
H15D	0.0427	0.0558	−0.3345	0.110*
H15E	0.0503	0.1321	−0.4212	0.110*
H15F	0.0827	0.2038	−0.3137	0.110*
N1A	0.4788 (2)	0.2973 (2)	0.41504 (17)	0.0444 (6)
N2A	0.6717 (2)	0.4155 (2)	0.35779 (17)	0.0447 (6)
N1B	0.5330 (2)	0.1304 (2)	0.28494 (16)	0.0401 (5)
N2B	0.5205 (2)	0.1561 (2)	0.12268 (17)	0.0432 (5)
O3A	1.0086 (3)	0.6354 (3)	0.04856 (18)	0.0750 (7)
O3B	0.2445 (2)	0.1762 (3)	−0.32803 (18)	0.0791 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ru1	0.03213 (14)	0.05153 (16)	0.05271 (16)	0.02061 (11)	0.01980 (11)	0.01231 (11)
C1	0.0428 (18)	0.064 (2)	0.070 (2)	0.0255 (17)	0.0274 (17)	0.0147 (18)
C2	0.0343 (15)	0.061 (2)	0.0535 (18)	0.0272 (15)	0.0132 (13)	0.0102 (16)
Cl1	0.0389 (4)	0.0765 (5)	0.0747 (5)	0.0333 (4)	0.0263 (4)	0.0163 (4)
Cl2	0.0516 (5)	0.0640 (5)	0.0789 (6)	0.0235 (4)	0.0326 (4)	0.0275 (4)
O1	0.0672 (17)	0.0851 (19)	0.0809 (18)	0.0162 (15)	0.0170 (14)	−0.0139 (16)
O2	0.0550 (14)	0.0795 (17)	0.0804 (16)	0.0373 (13)	0.0258 (12)	0.0357 (14)
C1A	0.0469 (17)	0.0600 (19)	0.0585 (19)	0.0285 (15)	0.0283 (15)	0.0204 (16)
C2A	0.069 (2)	0.068 (2)	0.0544 (18)	0.0418 (19)	0.0362 (17)	0.0251 (17)
C3A	0.067 (2)	0.062 (2)	0.0486 (17)	0.0351 (18)	0.0203 (16)	0.0111 (16)
C4A	0.0523 (19)	0.060 (2)	0.0564 (19)	0.0232 (17)	0.0129 (16)	0.0026 (16)
C5A	0.0436 (17)	0.0540 (19)	0.067 (2)	0.0165 (15)	0.0180 (16)	0.0064 (16)
C6A	0.0447 (18)	0.070 (2)	0.068 (2)	0.0247 (17)	0.0222 (16)	0.0186 (18)
C7A	0.0430 (18)	0.077 (2)	0.086 (3)	0.0240 (18)	0.0336 (19)	0.030 (2)
C8A	0.0507 (19)	0.058 (2)	0.075 (2)	0.0237 (16)	0.0334 (18)	0.0209 (18)
C9A	0.050 (2)	0.077 (2)	0.061 (2)	0.0167 (18)	0.0216 (17)	0.0160 (18)
C10A	0.0412 (18)	0.068 (2)	0.066 (2)	0.0099 (16)	0.0232 (16)	0.0114 (18)
C11A	0.0420 (16)	0.0411 (16)	0.0623 (19)	0.0154 (14)	0.0223 (15)	0.0089 (14)
C12A	0.0420 (16)	0.0448 (17)	0.0579 (18)	0.0216 (14)	0.0202 (14)	0.0106 (14)
C13A	0.0416 (15)	0.0462 (16)	0.0507 (16)	0.0274 (14)	0.0181 (13)	0.0128 (13)
C14A	0.0507 (18)	0.0512 (18)	0.0523 (17)	0.0307 (15)	0.0196 (14)	0.0135 (14)
C15A	0.073 (3)	0.141 (4)	0.081 (3)	0.041 (3)	0.039 (2)	0.056 (3)
C1B	0.0456 (17)	0.0522 (18)	0.0543 (17)	0.0249 (15)	0.0241 (14)	0.0151 (15)
C2B	0.0423 (16)	0.0587 (19)	0.0519 (17)	0.0277 (15)	0.0132 (14)	0.0151 (15)
C3B	0.0344 (15)	0.0553 (18)	0.0593 (18)	0.0236 (14)	0.0161 (14)	0.0131 (15)
C4B	0.0390 (16)	0.077 (2)	0.0642 (19)	0.0342 (16)	0.0236 (15)	0.0210 (17)
C5B	0.0436 (17)	0.085 (2)	0.0563 (18)	0.0356 (17)	0.0263 (15)	0.0218 (17)
C6B	0.0405 (17)	0.083 (2)	0.071 (2)	0.0263 (17)	0.0253 (16)	0.0341 (19)
C7B	0.051 (2)	0.103 (3)	0.066 (2)	0.034 (2)	0.0280 (17)	0.045 (2)
C8B	0.0450 (18)	0.064 (2)	0.064 (2)	0.0234 (16)	0.0170 (16)	0.0304 (17)
C9B	0.0412 (17)	0.075 (2)	0.070 (2)	0.0310 (17)	0.0161 (16)	0.0193 (18)
C10B	0.0456 (18)	0.082 (2)	0.0573 (19)	0.0342 (17)	0.0218 (15)	0.0187 (17)
C11B	0.0396 (16)	0.0541 (18)	0.0521 (17)	0.0221 (14)	0.0180 (14)	0.0162 (14)
C12B	0.0343 (15)	0.0475 (17)	0.0544 (17)	0.0180 (13)	0.0173 (13)	0.0104 (14)
C13B	0.0309 (14)	0.0391 (15)	0.0494 (16)	0.0161 (12)	0.0150 (12)	0.0061 (13)
C14B	0.0328 (14)	0.0477 (17)	0.0531 (17)	0.0207 (13)	0.0152 (13)	0.0088 (13)
C15B	0.049 (2)	0.085 (3)	0.084 (3)	0.0334 (19)	0.0133 (18)	0.032 (2)
N1A	0.0392 (13)	0.0518 (14)	0.0502 (14)	0.0245 (12)	0.0208 (11)	0.0170 (12)
N2A	0.0398 (13)	0.0461 (14)	0.0520 (14)	0.0201 (11)	0.0217 (11)	0.0111 (11)
N1B	0.0308 (11)	0.0446 (13)	0.0454 (13)	0.0172 (10)	0.0149 (10)	0.0107 (11)
N2B	0.0322 (12)	0.0485 (14)	0.0510 (14)	0.0197 (11)	0.0164 (11)	0.0107 (11)
O3A	0.0579 (15)	0.0945 (18)	0.0795 (16)	0.0291 (13)	0.0409 (13)	0.0427 (15)
O3B	0.0504 (14)	0.110 (2)	0.0777 (16)	0.0349 (14)	0.0209 (12)	0.0511 (15)

Geometric parameters (Å, º)

Ru1—C2	1.867 (3)	C15A—O3A	1.420 (4)
Ru1—C1	1.879 (4)	C15A—H15A	0.9600
Ru1—N1B	2.116 (2)	C15A—H15B	0.9600
Ru1—N1A	2.175 (2)	C15A—H15C	0.9600
Ru1—Cl1	2.4008 (8)	C1B—N1B	1.329 (3)
Ru1—Cl2	2.4389 (9)	C1B—C2B	1.395 (4)
C1—O1	1.131 (4)	C1B—H1B	0.9300
C2—O2	1.121 (4)	C2B—C3B	1.359 (4)
C1A—N1A	1.335 (3)	C2B—H2B	0.9300
C1A—C2A	1.387 (4)	C3B—C14B	1.400 (4)
C1A—H1A	0.9300	C3B—H3B	0.9300
C2A—C3A	1.357 (4)	C4B—C5B	1.345 (4)
C2A—H2A	0.9300	C4B—C14B	1.401 (4)
C3A—C14A	1.405 (4)	C4B—H4B	0.9300
C3A—H3A	0.9300	C5B—C12B	1.422 (4)
C4A—C5A	1.348 (4)	C5B—H5B	0.9300
C4A—C14A	1.410 (4)	C6B—C7B	1.378 (4)
C4A—H4A	0.9300	C6B—C11B	1.386 (4)
C5A—C12A	1.418 (4)	C6B—H6B	0.9300
C5A—H5A	0.9300	C7B—C8B	1.384 (4)
C6A—C7A	1.381 (4)	C7B—H7B	0.9300
C6A—C11A	1.407 (4)	C8B—O3B	1.366 (4)
C6A—H6A	0.9300	C8B—C9B	1.369 (4)
C7A—C8A	1.370 (5)	C9B—C10B	1.380 (4)
C7A—H7A	0.9300	C9B—H9B	0.9300
C8A—O3A	1.369 (4)	C10B—C11B	1.388 (4)
C8A—C9A	1.385 (4)	C10B—H10B	0.9300
C9A—C10A	1.382 (4)	C11B—C12B	1.482 (4)
C9A—H9A	0.9300	C12B—N2B	1.322 (3)
C10A—C11A	1.373 (4)	C13B—N2B	1.352 (3)
C10A—H10A	0.9300	C13B—N1B	1.371 (3)
C11A—C12A	1.481 (4)	C13B—C14B	1.417 (4)
C12A—N2A	1.332 (3)	C15B—O3B	1.430 (4)
C13A—N2A	1.347 (3)	C15B—H15D	0.9600
C13A—N1A	1.390 (3)	C15B—H15E	0.9600
C13A—C14A	1.407 (4)	C15B—H15F	0.9600
C2—Ru1—C1	90.63 (14)	O3A—C15A—H15C	109.5
C2—Ru1—N1B	95.79 (10)	H15A—C15A—H15C	109.5
C1—Ru1—N1B	94.98 (11)	H15B—C15A—H15C	109.5
C2—Ru1—N1A	91.44 (11)	N1B—C1B—C2B	124.1 (3)
C1—Ru1—N1A	177.08 (11)	N1B—C1B—H1B	117.9
N1B—Ru1—N1A	86.86 (8)	C2B—C1B—H1B	117.9
C2—Ru1—Cl1	85.94 (9)	C3B—C2B—C1B	118.4 (3)
C1—Ru1—Cl1	88.88 (9)	C3B—C2B—H2B	120.8
N1B—Ru1—Cl1	175.75 (6)	C1B—C2B—H2B	120.8

N1A—Ru1—Cl1	89.23 (6)	C2B—C3B—C14B	119.6 (3)
C2—Ru1—Cl2	175.65 (8)	C2B—C3B—H3B	120.2
C1—Ru1—Cl2	87.83 (10)	C14B—C3B—H3B	120.2
N1B—Ru1—Cl2	88.40 (6)	C5B—C4B—C14B	120.3 (3)
N1A—Ru1—Cl2	89.96 (6)	C5B—C4B—H4B	119.9
Cl1—Ru1—Cl2	89.96 (3)	C14B—C4B—H4B	119.9
O1—C1—Ru1	177.3 (3)	C4B—C5B—C12B	119.7 (3)
O2—C2—Ru1	172.3 (3)	C4B—C5B—H5B	120.2
N1A—C1A—C2A	123.8 (3)	C12B—C5B—H5B	120.2
N1A—C1A—H1A	118.1	C7B—C6B—C11B	121.7 (3)
C2A—C1A—H1A	118.1	C7B—C6B—H6B	119.1
C3A—C2A—C1A	120.2 (3)	C11B—C6B—H6B	119.1
C3A—C2A—H2A	119.9	C6B—C7B—C8B	120.1 (3)
C1A—C2A—H2A	119.9	C6B—C7B—H7B	119.9
C2A—C3A—C14A	118.1 (3)	C8B—C7B—H7B	119.9
C2A—C3A—H3A	121.0	O3B—C8B—C9B	124.7 (3)
C14A—C3A—H3A	121.0	O3B—C8B—C7B	115.6 (3)
C5A—C4A—C14A	119.7 (3)	C9B—C8B—C7B	119.6 (3)
C5A—C4A—H4A	120.1	C8B—C9B—C10B	119.4 (3)
C14A—C4A—H4A	120.1	C8B—C9B—H9B	120.3
C4A—C5A—C12A	119.8 (3)	C10B—C9B—H9B	120.3
C4A—C5A—H5A	120.1	C9B—C10B—C11B	122.6 (3)
C12A—C5A—H5A	120.1	C9B—C10B—H10B	118.7
C7A—C6A—C11A	120.4 (3)	C11B—C10B—H10B	118.7
C7A—C6A—H6A	119.8	C6B—C11B—C10B	116.5 (3)
C11A—C6A—H6A	119.8	C6B—C11B—C12B	122.2 (3)
C8A—C7A—C6A	121.0 (3)	C10B—C11B—C12B	121.3 (3)
C8A—C7A—H7A	119.5	N2B—C12B—C5B	121.6 (3)
C6A—C7A—H7A	119.5	N2B—C12B—C11B	118.0 (2)
O3A—C8A—C7A	116.1 (3)	C5B—C12B—C11B	120.4 (3)
O3A—C8A—C9A	124.1 (3)	N2B—C13B—N1B	117.3 (2)
C7A—C8A—C9A	119.7 (3)	N2B—C13B—C14B	122.5 (2)
C10A—C9A—C8A	118.7 (3)	N1B—C13B—C14B	120.1 (2)
C10A—C9A—H9A	120.7	C3B—C14B—C4B	123.8 (3)
C8A—C9A—H9A	120.7	C3B—C14B—C13B	119.2 (3)
C11A—C10A—C9A	123.2 (3)	C4B—C14B—C13B	116.9 (3)
C11A—C10A—H10A	118.4	O3B—C15B—H15D	109.5
C9A—C10A—H10A	118.4	O3B—C15B—H15E	109.5
C10A—C11A—C6A	116.9 (3)	H15D—C15B—H15E	109.5
C10A—C11A—C12A	121.1 (3)	O3B—C15B—H15F	109.5
C6A—C11A—C12A	121.8 (3)	H15D—C15B—H15F	109.5
N2A—C12A—C5A	121.7 (3)	H15E—C15B—H15F	109.5
N2A—C12A—C11A	117.7 (3)	C1A—N1A—C13A	117.4 (2)
C5A—C12A—C11A	120.5 (3)	C1A—N1A—Ru1	117.4 (2)
N2A—C13A—N1A	116.4 (2)	C13A—N1A—Ru1	125.10 (18)
N2A—C13A—C14A	123.4 (3)	C12A—N2A—C13A	118.3 (2)
N1A—C13A—C14A	120.2 (2)	C1B—N1B—C13B	118.4 (2)
C3A—C14A—C13A	120.0 (3)	C1B—N1B—Ru1	117.34 (18)

C3A—C14A—C4A	123.1 (3)	C13B—N1B—Ru1	123.91 (18)
C13A—C14A—C4A	116.8 (3)	C12B—N2B—C13B	119.0 (2)
O3A—C15A—H15A	109.5	C8A—O3A—C15A	117.3 (3)
O3A—C15A—H15B	109.5	C8B—O3B—C15B	118.1 (3)
H15A—C15A—H15B	109.5		

N1A—C1A—C2A—C3A	−4.0 (5)	C9B—C10B—C11B—C12B	−176.9 (3)
C1A—C2A—C3A—C14A	2.9 (5)	C4B—C5B—C12B—N2B	2.3 (5)
C14A—C4A—C5A—C12A	1.9 (5)	C4B—C5B—C12B—C11B	−176.7 (3)
C11A—C6A—C7A—C8A	0.0 (6)	C6B—C11B—C12B—N2B	−179.8 (3)
C6A—C7A—C8A—O3A	178.2 (3)	C10B—C11B—C12B—N2B	−3.1 (4)
C6A—C7A—C8A—C9A	0.0 (6)	C6B—C11B—C12B—C5B	−0.8 (5)
O3A—C8A—C9A—C10A	−178.6 (3)	C10B—C11B—C12B—C5B	175.9 (3)
C7A—C8A—C9A—C10A	−0.5 (5)	C2B—C3B—C14B—C4B	−179.0 (3)
C8A—C9A—C10A—C11A	1.2 (6)	C2B—C3B—C14B—C13B	−0.1 (4)
C9A—C10A—C11A—C6A	−1.2 (5)	C5B—C4B—C14B—C3B	178.7 (3)
C9A—C10A—C11A—C12A	174.4 (3)	C5B—C4B—C14B—C13B	−0.3 (5)
C7A—C6A—C11A—C10A	0.6 (5)	N2B—C13B—C14B—C3B	−177.2 (3)
C7A—C6A—C11A—C12A	−175.0 (3)	N1B—C13B—C14B—C3B	2.6 (4)
C4A—C5A—C12A—N2A	−4.0 (5)	N2B—C13B—C14B—C4B	1.8 (4)
C4A—C5A—C12A—C11A	173.1 (3)	N1B—C13B—C14B—C4B	−178.4 (3)
C10A—C11A—C12A—N2A	22.8 (4)	C2A—C1A—N1A—C13A	−0.1 (4)
C6A—C11A—C12A—N2A	−161.9 (3)	C2A—C1A—N1A—Ru1	177.4 (2)
C10A—C11A—C12A—C5A	−154.4 (3)	N2A—C13A—N1A—C1A	−173.8 (2)
C6A—C11A—C12A—C5A	20.9 (4)	C14A—C13A—N1A—C1A	5.1 (4)
C2A—C3A—C14A—C13A	2.0 (4)	N2A—C13A—N1A—Ru1	8.8 (3)
C2A—C3A—C14A—C4A	179.5 (3)	C14A—C13A—N1A—Ru1	−172.28 (19)
N2A—C13A—C14A—C3A	172.7 (3)	C5A—C12A—N2A—C13A	1.4 (4)
N1A—C13A—C14A—C3A	−6.1 (4)	C11A—C12A—N2A—C13A	−175.7 (2)
N2A—C13A—C14A—C4A	−5.0 (4)	N1A—C13A—N2A—C12A	−178.1 (2)
N1A—C13A—C14A—C4A	176.2 (3)	C14A—C13A—N2A—C12A	3.1 (4)
C5A—C4A—C14A—C3A	−175.3 (3)	C2B—C1B—N1B—C13B	1.5 (4)
C5A—C4A—C14A—C13A	2.3 (5)	C2B—C1B—N1B—Ru1	−172.0 (2)
N1B—C1B—C2B—C3B	1.0 (5)	N2B—C13B—N1B—C1B	176.5 (2)
C1B—C2B—C3B—C14B	−1.6 (4)	C14B—C13B—N1B—C1B	−3.3 (4)
C14B—C4B—C5B—C12B	−1.6 (5)	N2B—C13B—N1B—Ru1	−10.4 (3)
C11B—C6B—C7B—C8B	0.5 (6)	C14B—C13B—N1B—Ru1	169.78 (19)
C6B—C7B—C8B—O3B	−177.5 (3)	C5B—C12B—N2B—C13B	−0.8 (4)
C6B—C7B—C8B—C9B	−0.4 (6)	C11B—C12B—N2B—C13B	178.3 (2)
O3B—C8B—C9B—C10B	176.9 (3)	N1B—C13B—N2B—C12B	178.9 (2)
C7B—C8B—C9B—C10B	0.1 (6)	C14B—C13B—N2B—C12B	−1.3 (4)
C8B—C9B—C10B—C11B	0.1 (6)	C7A—C8A—O3A—C15A	−173.9 (4)
C7B—C6B—C11B—C10B	−0.3 (5)	C9A—C8A—O3A—C15A	4.3 (5)
C7B—C6B—C11B—C12B	176.6 (3)	C9B—C8B—O3B—C15B	−6.4 (5)
C9B—C10B—C11B—C6B	0.0 (5)	C7B—C8B—O3B—C15B	170.5 (3)

cis-Dicarbonyldichloridobis[2-(2-methoxyphenyl)-1,8-naphthyridine-κN⁸]ruthenium(II) (Ru_B)

Crystal data

$[RuCl_2(C_{15}H_{12}N_2O)_2(CO)_2]$
$M_r = 700.54$
Monoclinic, $C2/c$
$a = 19.106$ (3) Å
$b = 12.1967$ (16) Å
$c = 29.420$ (4) Å
$\beta = 94.918$ (2)°
$V = 6830.5$ (17) Å^3
$Z = 8$
$F(000) = 2832$
$D_x = 1.362$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 999 reflections
$\theta = 4.5$–$46.9°$
$\mu = 0.66$ mm^{-1}
$T = 296$ K
Plate, yellow
0.27 × 0.26 × 0.05 mm

Data collection

Bruker SMART CCD area detector diffractometer
Radiation source: sealed tube
phi and ω scans
Absorption correction: empirical (using intensity measurements) (SADABS; Bruker, 2012)
$T_{min} = 0.819$, $T_{max} = 0.964$
26258 measured reflections
6683 independent reflections
4821 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 26.0°$, $\theta_{min} = 2.1°$
$h = -23 \rightarrow 23$
$k = -15 \rightarrow 15$
$l = -36 \rightarrow 36$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.103$
$S = 0.98$
6683 reflections
391 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.59$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)
17.6598 (0.0062) x + 4.4525 (0.0077) y - 5.5935 (0.0305) z = 6.8792 (0.0324)
* 0.0230 (0.0021) N1A * -0.0071 (0.0024) C1A * -0.0226 (0.0029) C2A * -0.0129 (0.0030) C3A * 0.0213 (0.0029) C14A * 0.0301 (0.0028) C4A * -0.0168 (0.0027) C5A * -0.0479 (0.0024) C12A * 0.0331 (0.0026) C13A
Rms deviation of fitted atoms = 0.0264
16.8111 (0.0161) x - 2.6580 (0.0200) y + 10.1581 (0.0481) z = 21.4846 (0.0347)
Angle to previous plane (with approximate esd) = 46.628 (0.084)
* -0.0085 (0.0025) C11A * 0.0106 (0.0027) C6A * -0.0044 (0.0031) C7A * -0.0041 (0.0033) C8A * 0.0062 (0.0032) C9A * 0.0001 (0.0029) C10A
Rms deviation of fitted atoms = 0.0066
15.7087 (0.0111) x - 2.7250 (0.0130) y + 13.2720 (0.0204) z = 19.8080 (0.0133)
Angle to previous plane (with approximate esd) = 6.689 (0.180)
* 0.0332 (0.0022) N1B * -0.0117 (0.0026) C1B * -0.0399 (0.0029) C2B * 0.0027 (0.0031) C3B * 0.0227 (0.0033) C14B * 0.0226 (0.0033) C4B * -0.0071 (0.0032) C5B * -0.0395 (0.0025) C12B * 0.0170 (0.0027) C13B
Rms deviation of fitted atoms = 0.0253
12.9586 (0.0229) x + 7.1267 (0.0168) y + 11.3506 (0.0425) z = 16.8405 (0.0261)
Angle to previous plane (with approximate esd) = 48.671 (0.109)
* -0.0167 (0.0026) C11B * 0.0056 (0.0029) C6B * 0.0126 (0.0032) C7B * -0.0201 (0.0032) C8B * 0.0087 (0.0028) C9B * 0.0098 (0.0026) C10B
Rms deviation of fitted atoms = 0.0132

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ru1	0.58887 (2)	0.30746 (2)	0.88488 (2)	0.04548 (10)
C1	0.56541 (19)	0.3277 (3)	0.82276 (13)	0.0574 (9)
C2	0.67357 (18)	0.2447 (2)	0.87104 (10)	0.0475 (8)
C1A	0.60203 (18)	0.3902 (3)	0.98273 (12)	0.0595 (9)
H1A	0.5823	0.4505	0.9672	0.071*
C2A	0.6143 (2)	0.3975 (3)	1.02998 (12)	0.0670 (10)
H2A	0.6022	0.4607	1.0452	0.080*
C3A	0.6440 (2)	0.3115 (3)	1.05355 (12)	0.0640 (10)
H3A	0.6523	0.3148	1.0851	0.077*
C4A	0.69308 (18)	0.1225 (3)	1.05043 (12)	0.0602 (9)
H4A	0.7054	0.1214	1.0817	0.072*
C5A	0.70469 (18)	0.0335 (3)	1.02466 (12)	0.0593 (9)
H5A	0.7242	−0.0296	1.0382	0.071*
C6A	0.67341 (19)	−0.1639 (3)	0.95871 (14)	0.0630 (9)
C7A	0.6776 (2)	−0.2493 (3)	0.92799 (16)	0.0853 (13)
H7A	0.6616	−0.3187	0.9352	0.102*
C8A	0.7050 (3)	−0.2322 (4)	0.88716 (17)	0.0973 (15)
H8A	0.7076	−0.2903	0.8669	0.117*
C9A	0.7287 (3)	−0.1303 (3)	0.87556 (14)	0.0911 (14)
H9A	0.7478	−0.1194	0.8479	0.109*
C10A	0.7237 (2)	−0.0444 (3)	0.90576 (13)	0.0696 (10)
H10A	0.7394	0.0248	0.8981	0.083*

C11A	0.69602 (17)	−0.0591 (3)	0.94685 (12)	0.0529 (8)
C12A	0.68695 (17)	0.0370 (2)	0.97698 (11)	0.0481 (8)
C13A	0.64815 (16)	0.2151 (2)	0.98181 (10)	0.0434 (7)
C14A	0.66220 (17)	0.2167 (3)	1.02955 (11)	0.0507 (8)
C15A	0.6313 (3)	−0.2821 (3)	1.01492 (19)	0.1098 (17)
H15A	0.5923	−0.3119	0.9961	0.165*
H15B	0.6198	−0.2790	1.0460	0.165*
H15C	0.6718	−0.3281	1.0130	0.165*
C1B	0.50260 (16)	0.1337 (3)	0.92418 (11)	0.0532 (8)
H1B	0.4954	0.1919	0.9437	0.064*
C2B	0.47464 (19)	0.0325 (3)	0.93435 (13)	0.0659 (10)
H2B	0.4489	0.0240	0.9595	0.079*
C3B	0.4857 (2)	−0.0534 (3)	0.90678 (13)	0.0709 (11)
H3B	0.4690	−0.1226	0.9136	0.085*
C4B	0.5346 (2)	−0.1225 (3)	0.83629 (15)	0.0778 (11)
H4B	0.5195	−0.1937	0.8410	0.093*
C5B	0.5680 (2)	−0.0985 (3)	0.79948 (14)	0.0765 (11)
H5B	0.5761	−0.1533	0.7786	0.092*
C6B	0.6738 (2)	−0.0260 (4)	0.73118 (14)	0.0803 (12)
C7B	0.6971 (3)	0.0002 (5)	0.68881 (16)	0.0978 (16)
H7B	0.7323	−0.0414	0.6772	0.117*
C8B	0.6683 (3)	0.0867 (5)	0.66446 (15)	0.0948 (15)
H8B	0.6824	0.1012	0.6356	0.114*
C9B	0.6189 (2)	0.1530 (4)	0.68186 (14)	0.0834 (12)
H9B	0.6012	0.2137	0.6656	0.100*
C10B	0.59576 (19)	0.1281 (3)	0.72396 (13)	0.0671 (10)
H10B	0.5623	0.1728	0.7358	0.081*
C11B	0.62107 (19)	0.0389 (3)	0.74870 (12)	0.0636 (10)
C12B	0.59090 (18)	0.0096 (3)	0.79207 (12)	0.0569 (9)
C13B	0.54800 (16)	0.0672 (2)	0.85893 (10)	0.0466 (7)
C14B	0.52218 (18)	−0.0383 (3)	0.86826 (12)	0.0596 (9)
C15B	0.7537 (3)	−0.1769 (5)	0.7428 (2)	0.161 (3)
H15D	0.7384	−0.2082	0.7137	0.241*
H15E	0.7646	−0.2345	0.7645	0.241*
H15F	0.7948	−0.1330	0.7400	0.241*
Cl1	0.64502 (5)	0.48319 (7)	0.88440 (3)	0.0669 (3)
Cl2	0.47757 (5)	0.39313 (7)	0.89944 (3)	0.0690 (3)
N1A	0.61669 (14)	0.30300 (19)	0.95858 (9)	0.0482 (6)
N2A	0.66171 (13)	0.1268 (2)	0.95616 (8)	0.0461 (6)
N1B	0.53889 (12)	0.15319 (19)	0.88859 (8)	0.0454 (6)
N2B	0.58110 (13)	0.0906 (2)	0.82106 (8)	0.0487 (6)
O1	0.55373 (16)	0.3485 (2)	0.78538 (9)	0.0877 (9)
O2	0.72585 (13)	0.21316 (19)	0.86071 (8)	0.0642 (6)
O3A	0.64634 (15)	−0.1747 (2)	0.99962 (10)	0.0864 (9)
O3B	0.69909 (17)	−0.1099 (3)	0.75803 (10)	0.1120 (12)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ru1	0.05552 (18)	0.03555 (15)	0.04620 (17)	0.00224 (11)	0.00919 (12)	−0.00144 (11)
C1	0.061 (2)	0.050 (2)	0.061 (2)	−0.0001 (16)	0.0049 (18)	0.0035 (17)
C2	0.058 (2)	0.0405 (19)	0.0447 (19)	−0.0079 (16)	0.0083 (16)	0.0006 (14)
C1A	0.078 (2)	0.0421 (19)	0.059 (2)	0.0034 (17)	0.0140 (18)	−0.0096 (16)
C2A	0.089 (3)	0.053 (2)	0.061 (2)	0.003 (2)	0.014 (2)	−0.0231 (18)
C3A	0.080 (3)	0.066 (2)	0.047 (2)	0.002 (2)	0.0067 (18)	−0.0135 (18)
C4A	0.070 (2)	0.060 (2)	0.049 (2)	−0.0021 (18)	−0.0037 (17)	0.0020 (17)
C5A	0.065 (2)	0.054 (2)	0.058 (2)	0.0025 (17)	−0.0009 (17)	0.0083 (17)
C6A	0.064 (2)	0.041 (2)	0.084 (3)	0.0075 (16)	0.009 (2)	0.0012 (18)
C7A	0.103 (3)	0.043 (2)	0.111 (4)	0.005 (2)	0.016 (3)	−0.009 (2)
C8A	0.136 (4)	0.051 (3)	0.104 (4)	0.021 (3)	0.004 (3)	−0.024 (3)
C9A	0.136 (4)	0.070 (3)	0.070 (3)	0.027 (3)	0.025 (3)	−0.007 (2)
C10A	0.095 (3)	0.047 (2)	0.068 (2)	0.0121 (19)	0.014 (2)	0.0005 (18)
C11A	0.055 (2)	0.0396 (18)	0.064 (2)	0.0075 (15)	0.0041 (17)	0.0001 (16)
C12A	0.0515 (19)	0.0389 (17)	0.055 (2)	−0.0022 (14)	0.0077 (15)	−0.0006 (15)
C13A	0.0464 (18)	0.0370 (17)	0.0479 (18)	−0.0026 (13)	0.0091 (14)	−0.0034 (14)
C14A	0.054 (2)	0.052 (2)	0.0466 (18)	−0.0085 (16)	0.0069 (15)	−0.0055 (16)
C15A	0.107 (4)	0.061 (3)	0.170 (5)	0.006 (2)	0.062 (3)	0.029 (3)
C1B	0.052 (2)	0.056 (2)	0.053 (2)	0.0008 (16)	0.0112 (16)	−0.0034 (16)
C2B	0.064 (2)	0.069 (3)	0.068 (2)	−0.0077 (19)	0.0221 (19)	0.008 (2)
C3B	0.078 (3)	0.050 (2)	0.086 (3)	−0.0123 (19)	0.015 (2)	0.007 (2)
C4B	0.099 (3)	0.043 (2)	0.093 (3)	−0.008 (2)	0.016 (2)	−0.008 (2)
C5B	0.093 (3)	0.056 (2)	0.083 (3)	0.000 (2)	0.021 (2)	−0.023 (2)
C6B	0.076 (3)	0.108 (4)	0.058 (2)	0.013 (2)	0.010 (2)	−0.029 (2)
C7B	0.081 (3)	0.146 (5)	0.069 (3)	0.005 (3)	0.021 (3)	−0.039 (3)
C8B	0.085 (3)	0.141 (5)	0.060 (3)	−0.032 (3)	0.017 (2)	−0.018 (3)
C9B	0.075 (3)	0.104 (3)	0.071 (3)	−0.021 (3)	0.005 (2)	−0.007 (2)
C10B	0.059 (2)	0.078 (3)	0.067 (2)	−0.011 (2)	0.0132 (19)	−0.009 (2)
C11B	0.056 (2)	0.079 (3)	0.056 (2)	−0.0017 (19)	0.0069 (18)	−0.022 (2)
C12B	0.055 (2)	0.055 (2)	0.061 (2)	0.0035 (16)	0.0052 (17)	−0.0130 (17)
C13B	0.0459 (18)	0.0420 (18)	0.0525 (19)	−0.0008 (14)	0.0074 (15)	−0.0034 (15)
C14B	0.062 (2)	0.049 (2)	0.068 (2)	−0.0028 (17)	0.0120 (19)	−0.0022 (17)
C15B	0.151 (6)	0.196 (7)	0.139 (5)	0.103 (5)	0.034 (4)	−0.027 (4)
Cl1	0.0905 (7)	0.0397 (5)	0.0714 (6)	−0.0093 (4)	0.0113 (5)	−0.0003 (4)
Cl2	0.0699 (6)	0.0575 (6)	0.0818 (6)	0.0190 (4)	0.0184 (5)	0.0029 (5)
N1A	0.0611 (17)	0.0344 (14)	0.0503 (15)	0.0008 (12)	0.0115 (13)	−0.0060 (12)
N2A	0.0532 (16)	0.0385 (15)	0.0471 (15)	0.0017 (12)	0.0070 (12)	−0.0030 (12)
N1B	0.0452 (15)	0.0423 (14)	0.0493 (15)	0.0020 (12)	0.0080 (12)	−0.0023 (12)
N2B	0.0486 (15)	0.0469 (16)	0.0509 (16)	−0.0011 (12)	0.0060 (12)	−0.0046 (12)
O1	0.118 (2)	0.083 (2)	0.0593 (17)	0.0010 (17)	−0.0108 (16)	0.0090 (15)
O2	0.0567 (15)	0.0662 (16)	0.0715 (17)	0.0041 (12)	0.0160 (13)	0.0074 (12)
O3A	0.107 (2)	0.0470 (16)	0.112 (2)	0.0017 (14)	0.0458 (19)	0.0099 (14)
O3B	0.118 (3)	0.141 (3)	0.079 (2)	0.068 (2)	0.0205 (18)	−0.022 (2)

Geometric parameters (Å, º)

Ru1—C1	1.861 (4)	C15A—O3A	1.423 (4)
Ru1—C2	1.867 (4)	C15A—H15A	0.9600
Ru1—N1B	2.117 (2)	C15A—H15B	0.9600
Ru1—N1A	2.188 (3)	C15A—H15C	0.9600
Ru1—Cl1	2.3974 (9)	C1B—N1B	1.326 (4)
Ru1—Cl2	2.4400 (9)	C1B—C2B	1.388 (5)
C1—O1	1.132 (4)	C1B—H1B	0.9300
C2—O2	1.136 (3)	C2B—C3B	1.353 (5)
C1A—N1A	1.322 (4)	C2B—H2B	0.9300
C1A—C2A	1.393 (5)	C3B—C14B	1.392 (5)
C1A—H1A	0.9300	C3B—H3B	0.9300
C2A—C3A	1.355 (5)	C4B—C5B	1.336 (5)
C2A—H2A	0.9300	C4B—C14B	1.426 (5)
C3A—C14A	1.414 (4)	C4B—H4B	0.9300
C3A—H3A	0.9300	C5B—C12B	1.412 (5)
C4A—C5A	1.353 (4)	C5B—H5B	0.9300
C4A—C14A	1.409 (5)	C6B—O3B	1.357 (5)
C4A—H4A	0.9300	C6B—C7B	1.396 (6)
C5A—C12A	1.415 (4)	C6B—C11B	1.414 (5)
C5A—H5A	0.9300	C7B—C8B	1.365 (6)
C6A—O3A	1.356 (4)	C7B—H7B	0.9300
C6A—C7A	1.385 (5)	C8B—C9B	1.375 (6)
C6A—C11A	1.403 (5)	C8B—H8B	0.9300
C7A—C8A	1.367 (6)	C9B—C10B	1.384 (5)
C7A—H7A	0.9300	C9B—H9B	0.9300
C8A—C9A	1.376 (6)	C10B—C11B	1.373 (5)
C8A—H8A	0.9300	C10B—H10B	0.9300
C9A—C10A	1.382 (5)	C11B—C12B	1.488 (5)
C9A—H9A	0.9300	C12B—N2B	1.329 (4)
C10A—C11A	1.372 (5)	C13B—N2B	1.358 (4)
C10A—H10A	0.9300	C13B—N1B	1.385 (4)
C11A—C12A	1.489 (4)	C13B—C14B	1.413 (4)
C12A—N2A	1.326 (4)	C15B—O3B	1.426 (5)
C13A—N2A	1.353 (4)	C15B—H15D	0.9600
C13A—N1A	1.381 (4)	C15B—H15E	0.9600
C13A—C14A	1.407 (4)	C15B—H15F	0.9600
C1—Ru1—C2	88.89 (14)	O3A—C15A—H15C	109.5
C1—Ru1—N1B	95.56 (12)	H15A—C15A—H15C	109.5
C2—Ru1—N1B	92.86 (11)	H15B—C15A—H15C	109.5
C1—Ru1—N1A	173.79 (12)	N1B—C1B—C2B	124.5 (3)
C2—Ru1—N1A	93.70 (11)	N1B—C1B—H1B	117.7
N1B—Ru1—N1A	89.95 (9)	C2B—C1B—H1B	117.7
C1—Ru1—Cl1	86.89 (11)	C3B—C2B—C1B	118.5 (3)
C2—Ru1—Cl1	88.22 (9)	C3B—C2B—H2B	120.8
N1B—Ru1—Cl1	177.34 (7)	C1B—C2B—H2B	120.8

N1A—Ru1—Cl1	87.55 (7)	C2B—C3B—C14B	120.0 (3)
C1—Ru1—Cl2	88.59 (11)	C2B—C3B—H3B	120.0
C2—Ru1—Cl2	177.36 (9)	C14B—C3B—H3B	120.0
N1B—Ru1—Cl2	88.16 (7)	C5B—C4B—C14B	119.7 (4)
N1A—Ru1—Cl2	88.74 (7)	C5B—C4B—H4B	120.2
Cl1—Ru1—Cl2	90.88 (3)	C14B—C4B—H4B	120.2
O1—C1—Ru1	174.2 (3)	C4B—C5B—C12B	120.4 (3)
O2—C2—Ru1	174.9 (3)	C4B—C5B—H5B	119.8
N1A—C1A—C2A	124.3 (3)	C12B—C5B—H5B	119.8
N1A—C1A—H1A	117.9	O3B—C6B—C7B	124.6 (4)
C2A—C1A—H1A	117.9	O3B—C6B—C11B	116.1 (4)
C3A—C2A—C1A	119.2 (3)	C7B—C6B—C11B	119.3 (5)
C3A—C2A—H2A	120.4	C8B—C7B—C6B	120.0 (4)
C1A—C2A—H2A	120.4	C8B—C7B—H7B	120.0
C2A—C3A—C14A	119.2 (3)	C6B—C7B—H7B	120.0
C2A—C3A—H3A	120.4	C7B—C8B—C9B	121.2 (4)
C14A—C3A—H3A	120.4	C7B—C8B—H8B	119.4
C5A—C4A—C14A	119.5 (3)	C9B—C8B—H8B	119.4
C5A—C4A—H4A	120.2	C8B—C9B—C10B	119.1 (5)
C14A—C4A—H4A	120.2	C8B—C9B—H9B	120.5
C4A—C5A—C12A	119.6 (3)	C10B—C9B—H9B	120.5
C4A—C5A—H5A	120.2	C11B—C10B—C9B	121.6 (4)
C12A—C5A—H5A	120.2	C11B—C10B—H10B	119.2
O3A—C6A—C7A	123.6 (4)	C9B—C10B—H10B	119.2
O3A—C6A—C11A	117.2 (3)	C10B—C11B—C6B	118.7 (4)
C7A—C6A—C11A	119.1 (4)	C10B—C11B—C12B	120.0 (3)
C8A—C7A—C6A	120.4 (4)	C6B—C11B—C12B	121.3 (4)
C8A—C7A—H7A	119.8	N2B—C12B—C5B	122.2 (3)
C6A—C7A—H7A	119.8	N2B—C12B—C11B	117.3 (3)
C7A—C8A—C9A	121.0 (4)	C5B—C12B—C11B	120.3 (3)
C7A—C8A—H8A	119.5	N2B—C13B—N1B	116.7 (3)
C9A—C8A—H8A	119.5	N2B—C13B—C14B	123.1 (3)
C8A—C9A—C10A	118.9 (4)	N1B—C13B—C14B	120.2 (3)
C8A—C9A—H9A	120.6	C3B—C14B—C13B	119.1 (3)
C10A—C9A—H9A	120.6	C3B—C14B—C4B	124.4 (3)
C11A—C10A—C9A	121.4 (4)	C13B—C14B—C4B	116.5 (3)
C11A—C10A—H10A	119.3	O3B—C15B—H15D	109.5
C9A—C10A—H10A	119.3	O3B—C15B—H15E	109.5
C10A—C11A—C6A	119.2 (3)	H15D—C15B—H15E	109.5
C10A—C11A—C12A	119.7 (3)	O3B—C15B—H15F	109.5
C6A—C11A—C12A	121.0 (3)	H15D—C15B—H15F	109.5
N2A—C12A—C5A	122.0 (3)	H15E—C15B—H15F	109.5
N2A—C12A—C11A	115.6 (3)	C1A—N1A—C13A	117.5 (3)
C5A—C12A—C11A	122.4 (3)	C1A—N1A—Ru1	117.9 (2)
N2A—C13A—N1A	116.0 (3)	C13A—N1A—Ru1	124.62 (19)
N2A—C13A—C14A	122.6 (3)	C12A—N2A—C13A	118.7 (3)
N1A—C13A—C14A	121.4 (3)	C1B—N1B—C13B	117.7 (3)
C13A—C14A—C4A	117.4 (3)	C1B—N1B—Ru1	117.9 (2)

C13A—C14A—C3A	118.4 (3)	C13B—N1B—Ru1	124.0 (2)
C4A—C14A—C3A	124.1 (3)	C12B—N2B—C13B	118.1 (3)
O3A—C15A—H15A	109.5	C6A—O3A—C15A	118.2 (3)
O3A—C15A—H15B	109.5	C6B—O3B—C15B	118.8 (4)
H15A—C15A—H15B	109.5		

N1A—C1A—C2A—C3A	1.0 (6)	O3B—C6B—C11B—C12B	−5.4 (6)
C1A—C2A—C3A—C14A	0.4 (6)	C7B—C6B—C11B—C12B	175.5 (4)
C14A—C4A—C5A—C12A	1.2 (5)	C4B—C5B—C12B—N2B	0.6 (6)
O3A—C6A—C7A—C8A	179.4 (4)	C4B—C5B—C12B—C11B	−173.4 (4)
C11A—C6A—C7A—C8A	1.6 (6)	C10B—C11B—C12B—N2B	−45.4 (5)
C6A—C7A—C8A—C9A	−0.2 (7)	C6B—C11B—C12B—N2B	137.1 (4)
C7A—C8A—C9A—C10A	−0.8 (7)	C10B—C11B—C12B—C5B	128.8 (4)
C8A—C9A—C10A—C11A	0.4 (7)	C6B—C11B—C12B—C5B	−48.6 (5)
C9A—C10A—C11A—C6A	1.0 (6)	C2B—C3B—C14B—C13B	0.9 (6)
C9A—C10A—C11A—C12A	−175.8 (4)	C2B—C3B—C14B—C4B	−177.8 (4)
O3A—C6A—C11A—C10A	−179.9 (3)	N2B—C13B—C14B—C3B	−176.7 (3)
C7A—C6A—C11A—C10A	−2.0 (5)	N1B—C13B—C14B—C3B	2.0 (5)
O3A—C6A—C11A—C12A	−3.2 (5)	N2B—C13B—C14B—C4B	2.1 (5)
C7A—C6A—C11A—C12A	174.7 (3)	N1B—C13B—C14B—C4B	−179.2 (3)
C4A—C5A—C12A—N2A	2.8 (5)	C5B—C4B—C14B—C3B	177.5 (4)
C4A—C5A—C12A—C11A	−177.9 (3)	C5B—C4B—C14B—C13B	−1.2 (6)
C10A—C11A—C12A—N2A	42.6 (4)	C2A—C1A—N1A—C13A	−2.1 (5)
C6A—C11A—C12A—N2A	−134.1 (3)	C2A—C1A—N1A—Ru1	177.5 (3)
C10A—C11A—C12A—C5A	−136.7 (4)	N2A—C13A—N1A—C1A	179.3 (3)
C6A—C11A—C12A—C5A	46.5 (5)	C14A—C13A—N1A—C1A	1.9 (4)
N2A—C13A—C14A—C4A	1.5 (5)	N2A—C13A—N1A—Ru1	−0.3 (4)
N1A—C13A—C14A—C4A	178.7 (3)	C14A—C13A—N1A—Ru1	−177.7 (2)
N2A—C13A—C14A—C3A	−177.9 (3)	C5A—C12A—N2A—C13A	−4.6 (4)
N1A—C13A—C14A—C3A	−0.6 (5)	C11A—C12A—N2A—C13A	176.0 (3)
C5A—C4A—C14A—C13A	−3.2 (5)	N1A—C13A—N2A—C12A	−174.9 (3)
C5A—C4A—C14A—C3A	176.1 (3)	C14A—C13A—N2A—C12A	2.4 (4)
C2A—C3A—C14A—C13A	−0.5 (5)	C2B—C1B—N1B—C13B	1.7 (5)
C2A—C3A—C14A—C4A	−179.8 (3)	C2B—C1B—N1B—Ru1	−171.4 (3)
N1B—C1B—C2B—C3B	1.1 (5)	N2B—C13B—N1B—C1B	175.6 (3)
C1B—C2B—C3B—C14B	−2.4 (6)	C14B—C13B—N1B—C1B	−3.2 (4)
C14B—C4B—C5B—C12B	−0.1 (6)	N2B—C13B—N1B—Ru1	−11.8 (4)
O3B—C6B—C7B—C8B	−179.8 (4)	C14B—C13B—N1B—Ru1	169.4 (2)
C11B—C6B—C7B—C8B	−0.9 (7)	C5B—C12B—N2B—C13B	0.2 (5)
C6B—C7B—C8B—C9B	3.4 (7)	C11B—C12B—N2B—C13B	174.3 (3)
C7B—C8B—C9B—C10B	−3.0 (7)	N1B—C13B—N2B—C12B	179.7 (3)
C8B—C9B—C10B—C11B	0.0 (6)	C14B—C13B—N2B—C12B	−1.6 (5)
C9B—C10B—C11B—C6B	2.4 (6)	C7A—C6A—O3A—C15A	10.0 (6)
C9B—C10B—C11B—C12B	−175.1 (3)	C11A—C6A—O3A—C15A	−172.2 (4)
O3B—C6B—C11B—C10B	177.1 (4)	C7B—C6B—O3B—C15B	0.5 (7)
C7B—C6B—C11B—C10B	−1.9 (6)	C11B—C6B—O3B—C15B	−178.5 (5)