

Arene ruthenium complexes with chiral Schiff bases derived from pyridine-2-carboxaldehyde or 2-acetylpyridine

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Abstract

The Schiff bases (LL') formed from pyridine-2-carboxaldehyde or 2-acetyl pyridine and *S*-1-phenylethylamine react with [Ru(mes)Cl₂]₂ (mes = η^6 -C₆H₃Me₃-1,3,5) to form diastereomeric salts [Ru(mes)Cl(LL')][BF₄]. Crystallisation gives a single diastereomer, (*S*_{Ru}*S*_C) in each case, which have been characterised by X-ray diffraction; the conformation of the phenylethyl group is different to related η^6 -benzene complexes. The configuration at the metal is solvent dependent, it is stable in CDCl₃ but epimerisation occurs in D₂O. © 1997 Elsevier Science S.A.

1. Introduction

Half-sandwich complexes have proved to be extremely useful in stoichiometric and catalytic asymmetric synthesis and have therefore attracted much study [1–5]. In addition, the four-coordinate, pseudo-tetrahedral geometry makes them particularly suitable for investigation of the stereochemistry of reactions at the metal centre [6]. Many studies of cyclopentadienyl ruthenium(II) complexes with bidentate ligands have shown that substitution reactions occur predominantly with retention of configuration at the metal [7]. Until recently far fewer studies had been carried out on arene–ruthenium complexes.

A number of arene–ruthenium complexes with simple bidentate amino acids are now known and in each case two diastereomers are found in solution [8–14]. Mandal and Chakravarty synthesised arene ruthenium complexes containing N,N' and N,O donor Schiff base ligands derived from either 2-formyl pyridine or salicylaldehyde and commented on the stereochemistry of the substitution reactions [15–19]. Brunner has since reported more detailed studies on a number of these and related complexes and shown that some of the assignments of absolute configurations and the conclusions

regarding stereochemistry of substitution reactions were flawed [20,21]. The confusion arises due to the configuration at ruthenium being unstable in solution and the rate of inversion at the metal being slow on the NMR timescale ($k < 10^{-1} \text{ s}^{-1}$) but relatively fast on a chemical timescale ($k > 10^{-3} \text{ s}^{-1}$). Thus, dissolution of a single diastereomer at room temperature can lead to observation of two diastereomers in the NMR spectrum since as many as three half-lives may have elapsed before the spectrum is actually run and thus the isomerisation could be 87.5% of the way to the equilibrium position. Given the accuracy with which integrals are usually measured and that in most cases the more favourable diastereomer is the one that is crystallised the difference between the ratio of isomers observed when the spectrum is run and the true equilibrium position is likely to be small hence no further changes are observed. Brunner exposed this mistake by dissolving single diastereomers of salicylaldiminato complexes at low temperature and found that the diastereomers are able to interconvert relatively easily even at low temperatures (-40°C) in a non-coordinating solvent (CH₂Cl₂). Most of the studies so far have been on diastereomeric species since these are easily distinguished by NMR, though we have reported that for an arene ruthenium ethylpyranato complex and a related Cp^{*}Rh species the rate of interconversion of two enantiomers is fast on the NMR timescale [22,23]. Further work on the mechanism of these isomerisations is currently in progress. We

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report here a case where the interconversion of two diastereomers is very slow in CDCl_3 .

2. Results and discussion

The complexes **1a** and **2a** were prepared by refluxing the relevant ligand with $[\text{Ru}(\text{mes})\text{Cl}_2]_2$ in dichloromethane. The ^1H NMR spectra in CDCl_3 showed the presence of two diastereomers in each case however, all attempts to separate the diastereomers by crystallisation of **1a** and **2a** in common solvent mixtures failed. Therefore, both compounds were treated with one equivalent of AgBF_4 to form the corresponding BF_4 salts **1b** and **2b**. These can be prepared directly from $[\text{Ru}(\text{mes})\text{Cl}_2]_2$ by refluxing with the appropriate ligand in the presence of NaBF_4 in methanol. Complexes **1b** and **2b** were fully characterised by ^1H NMR, FAB mass spectroscopy, elemental analysis and X-ray diffraction. The ^1H NMR spectra showed the presence of two diastereomers in a 2.7:1 ratio for **1b** and 2:1 ratio for **2b**. In each case, the major diastereomer could be crystallised and the crystals were studied by X-ray diffraction. Crystal data are shown in Table 1, selected bond distances and angles in Table 2 (**1b**) and Table 3 (**2b**), and the structures of the cations are shown in Fig.

Table 2

Selected bond lengths (Å) and angles (°) for complex **1b**

	Molecule 1	Molecule 2
Ru(1)–N(1)	2.103(11)	2.075(9)
Ru(1)–N(2)	2.095(10)	2.111(10)
Ru(1)–Cl(1)	2.401(3)	2.386(4)
Ru(1)–C(15)	2.217(14)	2.254(12)
Ru(1)–C(16)	2.168(13)	2.227(13)
Ru(1)–C(17)	2.23(2)	2.20(2)
Ru(1)–C(18)	2.18(2)	2.221(13)
Ru(1)–C(19)	2.217(13)	2.21(2)
Ru(1)–C(20)	2.204(14)	2.241(11)
N(1)–C(5)	1.35(2)	1.336(14)
C(5)–C(6)	1.45(2)	1.46(2)
N(2)–C(6)	1.27(2)	1.303(14)
N(2)–C(7)	1.47(2)	1.47(2)
N(1)–Ru(1)–N(2)	77.1(4)	77.0(4)
N(1)–Ru(1)–Cl(1)	83.1(3)	82.1(3)
N(2)–Ru(1)–Cl(1)	85.6(3)	85.8(3)

1 (**1b**) and Fig. 2 (**2b**). Only one diastereoisomer was present in each case, the configuration at carbon is assumed to be *S* as in the chiral amine used to synthesise the ligand and the ruthenium centre also has the S_{Ru} configuration, specified with the priority sequence $\eta^6\text{-C}_6\text{H}_6 > \text{Cl} > \text{N}(\text{imine}) > \text{N}(\text{pyridine})$ [24,25]. For **1b** two independent molecules were found in the unit cell

Table 1

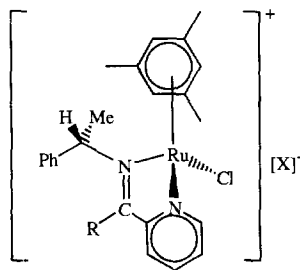
Summary of crystal data, data collection and structure refinement^a for complexes **1b** and **2b**

	1b	2b
Formula	$\text{C}_{23}\text{H}_{26}\text{BClF}_4\text{N}_2\text{Ru}$	$\text{C}_{24}\text{H}_{28}\text{BClF}_4\text{N}_2\text{Ru}$
<i>M</i>	553.8	567.8
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1$
<i>a</i> , Å	8.556(2)	7.459(1)
<i>b</i> , Å	19.176(2)	11.549(1)
<i>c</i> , Å	29.229(2)	14.645(1)
β°		100.74(1)
Volume <i>V</i> (Å ³)	4795(1)	1239.5(2)
Number of molecules in unit cell <i>Z</i>	8 (4 for each unique molecule)	2
Density (g cm ⁻³)	1.534	1.521
<i>F</i> (000)	2240	576
μ (mm ⁻¹)	0.809	0.785
Crystal colour, habit	Orange needle	Orange block
Crystal dimensions (mm)	size $0.6 \times 0.18 \times 0.10$	$0.52 \times 0.28 \times 0.10$
2θ range	5.0–50.0	4–54
Scan type	Omega	Omega
<i>h,k,l</i> ranges	–1 to 9, –1 to 21, –1 to 34	–1 to 9, –1 to 14, –18 to 18
Total data	5357	3819
Unique data (R_{int})	5111 ($R_{\text{int}} = 0.0236$)	3114 ($R_{\text{int}} = 0.0224$)
'Observed' data [$F > 4\sigma(F)$], N_o	3891	2832
Least squares variables, N_v	526	298
R_1^b	0.0625	0.037
wR_2^b (all data)	0.159	0.098
Goodness of fit S^b	1.177	1.059
Flack parameter	–0.109 (0.086)	0.025 (0.057)

^aSiemens P4 diffractometer; Mo– K_α radiation ($\lambda = 0.71073$ Å); 293 K.

^b $R_1 = \sum [F_o - F_c] / \sum F_o$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$; $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ where *n* = number of reflections and *p* = total number of parameters refined.

which, combined with the rather large standard deviations, makes detailed comparison with other structures



R = H, X = Cl (1a), X = BF₄ (1b)
R = Me, X = Cl (2a), X = BF₄ (2b)

less useful. The Ru–Cl, Ru–N(1) and Ru–N(2) bond lengths and N(1)–Ru–N(2) chelate angle in **1b** and **2b** are statistically the same as those found previously in [RuCl(LL')(p-cymene)]Cl (LL' = the Schiff base derived from pyridine-2-carboxaldehyde and p-toluidine) [18].

The orientation of the 1-phenylethyl substituent with respect to the [Ru(mes)Cl(LL')] moiety is similar in both molecules. In related complexes with the Schiff base formed from salicylaldehyde and 1-(S)-phenylethylamine, Brunner concluded that in the thermodynamically more stable diastereomers the C–H bond of the 1-phenylethyl substituent is oriented towards the unidentate ligand to minimise steric hindrance, whilst the phenyl takes up a face-on orientation relative to the η⁶-arene ring ('β-phenyl effect') [21]. Similarly, in [Ru(η⁶-C₆H₆)Cl(LL')] (LL' = the anion of 2-(S)-N-(1-phenylethyl)pyrrole-carbaldimine) it was argued that a 'β-phenyl' interaction was possible in both diastere-

Table 3

Selected bond lengths (Å) and angles (°) for complex **2b**

Ru(1)–N(1)	2.066(5)
Ru(1)–N(2)	2.086(5)
Ru(1)–Cl(1)	2.397(2)
Ru(1)–C(16)	2.243(7)
Ru(1)–C(17)	2.267(5)
Ru(1)–C(18)	2.192(5)
Ru(1)–C(19)	2.195(6)
Ru(1)–C(20)	2.198(7)
Ru(1)–C(21)	2.215(9)
N(1)–C(5)	1.347(9)
C(5)–C(6)	1.498(8)
N(2)–C(6)	1.277(8)
N(2)–C(8)	1.489(6)
N(1)–Ru(1)–N(2)	76.3(2)
N(1)–Ru(1)–Cl(1)	85.45(14)
N(2)–Ru(1)–Cl(1)	84.29(13)

omers [26]. There is no evidence for a 'β-phenyl effect' in the solid state for either **1b** or **2b** and the small differences in chemical shift (< 0.2 ppm) between the aromatic signals for the two diastereomers of **1b** and of **2b** in CDCl₃ give no additional clues to the presence or absence of such effects in solution. The absence of a 'β-phenyl effect' in **1b** and **2b** may be because the η⁶-arene is mesitylene and there will be considerably greater steric repulsions with the methyl groups than is the case with benzene. In addition, in neither structure is the C–H bond of the phenylethyl substituent directed towards the unidentate ligand, i.e., Cl. In both cases the methyl is directed towards the chloride particularly in **1b**. Brunner has previously suggested that there is less steric hindrance between the methyl and the chloride for a 5-membered chelate ring rather than a 6-membered one in salicylaldiminato complexes [26]. In **1b** the

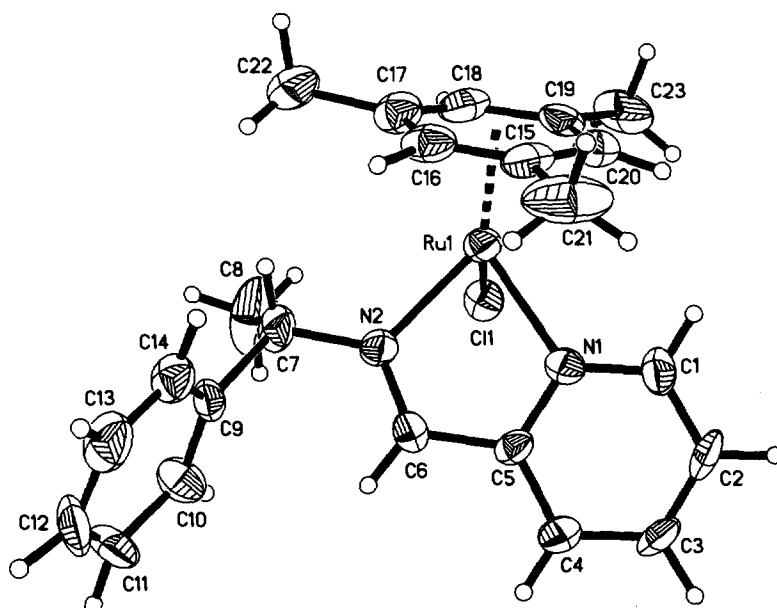


Fig. 1. Molecular structure of the cation of **1b** showing 30% probability ellipsoids for all non hydrogen atoms.

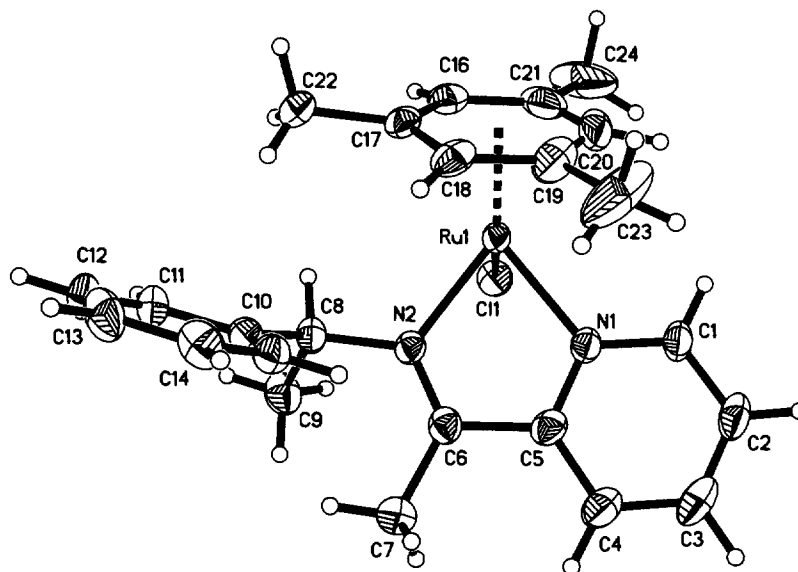


Fig. 2. Molecular structure of the cation of **2b** showing 30% probability ellipsoids for all non hydrogen atoms.

dihedral angle between the imine carbon and the methyl of the phenylethyl C(6)–N(2)–C(7)–C(9) is 98° for molecule 1 and 122° for molecule 2 which, particularly for molecule 2, gives a conformation in which the phenyl substituent is almost eclipsed and face-on to the imine hydrogen. For **2b** the corresponding angle C(6)–N(2)–C(8)–C(10) is 56° with the C(8)–H bond being nearly eclipsed with the Ru–N(2) this presumably minimises any unfavourable interactions between the phenylethyl and the imine methyl.

The ^1H NMR spectra of recrystallised samples of **1b** or **2b** in chloroform showed the presence of a very small amount of the minor diastereomer ($< 5\%$) and the amount didn't change significantly even after 2–3 days. The ^1H NMR spectra of the mother liquors, now enriched in the more soluble isomer, showed a very different ratio of isomers which also did not change significantly after 2–3 days in solution. This suggests that in this case interconversion of the two diastereomers is relatively slow even on a chemical timescale in CDCl_3 .

When crystals of **1b** are dissolved in D_2O the ^1H NMR spectrum shows the presence of three or four species due to two diastereomers each with either D_2O or chloride co-ordinated as has been observed previously for amino acidate complexes [13]. Addition of NaCl simplifies the spectrum, only two species, i.e., the two diastereomers with chloride coordinated, being observed. In contrast to the observations in CDCl_3 , the ratio of diastereomers in D_2O changes over time, even so it still takes many days for the diastereomers to reach equilibrium (final ratio 1.2:1). Complex **2b** dissolves poorly in D_2O , and is even less soluble with added NaCl hence the signals in D_2O cannot be fully assigned and the diastereoisomer ratio cannot be calculated.

We have shown that the rate of interconversion of

the diastereomers of **1b** and **2b** is dependent on the solvent. The configuration at ruthenium for these complexes is stable in chloroform for days. Brunner previously found that for two monoanionic ligands an N–N donor gave a slower rate of isomerisation than an N–O donor [26]. Our complexes have even greater configurational stability possibly because using a neutral N–N donor means that loss of chloride from a cation will be less favoured.

3. Experimental

Petroleum ether (b.p. $40\text{--}60^\circ\text{C}$) and diethyl ether were dried by refluxing over purple sodium/benzophenone under nitrogen, dichloromethane by refluxing over calcium hydride and methanol from magnesium turnings and iodine. The complex $[\text{Ru}(\text{mes})\text{Cl}_2]_2$ [27], was made by the literature procedure the Schiff bases were made by refluxing the equivalent amounts of the ketone or aldehyde with the amine in ethanol for several hours. The reactions described were carried out under nitrogen; however, once isolated as pure solids the compounds are air-stable and precautions for their storage are unnecessary.

^1H NMR spectra were recorded on a Bruker AM300 spectrometer. Microanalyses were performed by Butterworth laboratories, Middlesex. FAB mass spectra were recorded on a Kratos Concept mass spectrometer using a NOBA matrix.

4. Preparation of $[\text{Ru}(\text{mes})\text{Cl}\{\text{C}_5\text{H}_4\text{N}-2\text{-C}(\text{H})=\text{N}(\text{CHMePh})\}]\text{BF}_4$ (**1b**)

A mixture of $[\text{Ru}(\text{mes})\text{Cl}_2]_2$ (150 mg; 0.26 mmol), the Schiff base $\text{C}_5\text{H}_4\text{N}-2\text{-C}(\text{H})=\text{N}(\text{CHMePh})$ (109 mg; 0.52 mmol) and NaBF_4 (57 mg; 0.52 mmol) in methanol

(20 cm³) was refluxed for 4 h during which time the solution turned from orange to brown. The mixture was rotary evaporated to dryness, dissolved in dichloromethane and filtered through celite. Rotary evaporation of the filtrate and drying in vacuo gave **1b** as a brown solid (250 mg, 87%). Found: C, 48.66; H, 4.90; N, 4.75. C₂₃H₂₆BClF₄N₂Ru · H₂O requires C, 48.31; H, 4.94; N, 4.89%. FAB MS: *m/z* 467 (M⁺). ¹H NMR (CDCl₃): δ (ppm, *J*(Hz), signals for the minor isomer are given in parentheses) 1.83(1.95) (3H, d, *J* 7, CHMe); 2.15(2.14) (9H, s, C₆Me₃); 5.54(5.52) (3H, s, C₆H₃); 5.68* (1H, q, *J* 7, CHMe); 7.3–7.5* (5H, m, Ph); 7.62* (1H, dt, *J* 1.5, 6.5, pyr-H) 7.76* (1H, d, *J* 7, pyr-H) 7.88* (1H, dt, *J* 1, 7.5, pyr-H); 7.98(8.43) (1H, s, N=CH); 9.20(9.12) (1H, d, *J* 5, pyr-H). * Signals for the minor isomer are obscured by the major isomer.

5. Preparation of [Ru(mes)Cl{C₅H₄N-2-C(Me)=N(CHMePh)}][BF₄] (**2b**)

This was prepared in a similar way on the same scale using the Schiff base C₅H₄N-2-C(Me)=N(CHMePh) (117 mg; 0.52 mmol) and gave **2b** as a brown solid (252 mg, 93%). Found: C, 50.12; H, 4.57; N, 4.93%. C₂₄H₂₈BClF₄N₂Ru requires C, 50.77; H, 4.97; N, 4.93%. FAB MS: *m/z* 481 (M⁺). ¹H NMR (CDCl₃): δ (ppm, *J*(Hz), signals for the minor isomer are given in parentheses) 1.90* (3H, d, *J* 7, CHMe); 2.07(2.12) (9H, s, C₆Me₃); 2.32(2.26) (3H, s, N=CMe); 5.40(5.52) (3H, s, C₆H₃); 6.12(5.91) (1H, q, *J* 7, CHMe); 7.3–7.6* (5H, m, Ph); 7.69* (1H, dt, *J* 1.5, 6.5, pyr-H) 7.84* (1H, d, *J* 7, pyr-H) 7.97* (1H, dt, *J* 1.5, 8, pyr-H); 9.23* (1H, d, ³*J* 5, pyr-H). * Signals for the minor isomer are obscured by the major isomer.

6. Crystallography

Crystals of both complexes were grown from methanol ether. The details of the crystal structure determinations are summarised in Table 1. Data sets were corrected for Lorentz and polarisation effects and semi empirical absorption corrections based on ψ scan data were applied. The structures were solved by Patterson methods using the program SHELXTL-PC [28] and refined using full matrix least squares on F^2 with the program SHELXL 96 [29]. For both structures hydrogen atoms were included in calculated positions (C–H 0.96 Å) with isotropic displacement parameters set to 1.2 U_{eq} of the bonded atom. The BF₄[−] ions of both **1b** and **2b** were restrained to have approximate tetrahedral geometry with B–F and F...F set to 1.320(4) and 2.155(6) Å, respectively. All non hydrogen atoms were refined with anisotropic displacement parameters except the BF₄[−]

ions of **1b**. The displacement parameters of the F atoms of all BF₄[−] ions were high but satisfactory disordered models were not found. Tables of atomic coordinates, thermal parameters and complete bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre.

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