ChemComm

Kinetic control of stereoselectivity of halide substitution in arene ruthenium pyridyloxazoline complexes; a rare case of net inversion†

Adam J. Davenport, David L. Davies,* John Fawcett, Shaun A. Garratt and David R. Russell

Department of Chemistry, University of Leicester, Leicester, UK LE1 7RH. E-mail: dld3@le.ac.uk

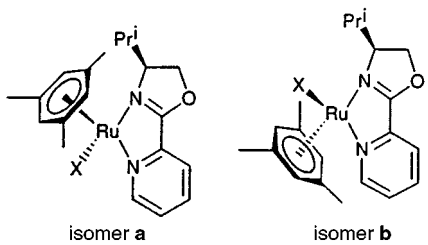
Received (in Cambridge, UK) 30th September 1999, Accepted 19th October 1999

Reaction of [RuCl(Pr^i-pymox)(η^6-mes)]$^+$ 1b [Pr^i-pymox = 4-isopropyl-2-(2-pyridyl)-1,3-oxazoline, mes = 1,3,5-trimethylbenzene] with $AgSbF_6$ then with halide gives [RuX(Pr^i-pymox)(η^6-mes)]$^+$ (X = Cl 1, Br 2, I 3), each as a mixture of diastereomers, the kinetic product being formed preferentially with net inversion of configuration at the metal; the structures of 2a and 2b have been determined by X-ray crystallography.

The stable well defined geometry of half-sandwich complexes makes them useful substrates for the study of the mechanism, particularly the stereochemistry, of substitution reactions at a chiral metal centre.[1] In addition, arene ruthenium complexes are becoming increasingly important in asymmetric catalysis.[2] In order to optimise the enantioselection of such complexes it is important to understand the factors that control diastereoselectivity, the tendency for epimerisation at the metal and the stereochemistry of substitution reactions.

Arene ruthenium(II) complexes have low-spin d^6-configuration and ligand exchange is usually dissociative, as found for anation of $[Ru(H_2O)(bipy)(\eta^6\text{-arene})]^{2+}$.[3] The stereoselectivity of substitution is determined by the stereochemical stability of the five-coordinate intermediate, partial epimerisation at the metal occurs in some cases.[4] In many cases kinetic control of asymmetric induction is hard to prove since the interconversion of the product diastereomers is relatively facile under the reaction conditions, this has lead to erroneous conclusions about stereoselectivity.[5] Nelson and coworkers reported that substitution of some cyclometallated arene ruthenium complexes occurred, in all cases, with preferential retention of configuration, and with very high selectivity in the case of halide exchange.[6]

Coordination of pyridyloxazolines to an '(arene)RuX' fragment can in principle give rise to two isomers (**a** and **b**). Treatment of $[RuCl_2(mes)]_2$ with Pr^i-pymox in refluxing methanol, gave $[RuCl(Pr^i\text{-pymox})(\eta^6\text{-mes})]SbF_6$ as one diastereomer which was shown by X-ray crystallography to have the isopropyl pointing towards the chloride (**1b**) rather than the π-bound ring.[7] Abstraction of chloride with $AgSbF_6$ in acetone–water gives $[Ru(H_2O)(Pr^i\text{-pymox})(\eta^6\text{-mes})][SbF_6]_2$ which reacts with KCl, KBr or NaI in methanol at room temperature to give the halide complexes $[RuX(Pr^i\text{-pymox})(\eta^6\text{-mes})]SbF_6$ (X = Cl **1**, Br **2**, I **3**).†



† ^{1}H NMR spectra and satisfactory elemental analyses are available as electronic supplementary information (ESI): See http://www.rsc.org/suppdata/cc/1999/2331/

The ^{1}H NMR spectrum of a crude sample of **2** shows the presence of two diastereomers in an approximate ratio of 75 : 25. Careful recrystallisation allowed separation of the two diastereomers and their structures were determined by X-ray diffraction.‡ Isomer **2b** (Fig. 1) has the isopropyl pointing towards the halide, the same as found previously for the chloride,[7] whilst isomer **2a** (Fig. 2) has the isopropyl pointing towards the π-bound arene. The Ru–N(1), Ru–N(2), distances and the N(1)–Ru–N(2) angle are statistically the same in each isomer and with the chloride **1b**.[7] The Ru–Br bond is slightly longer in isomer **2b**

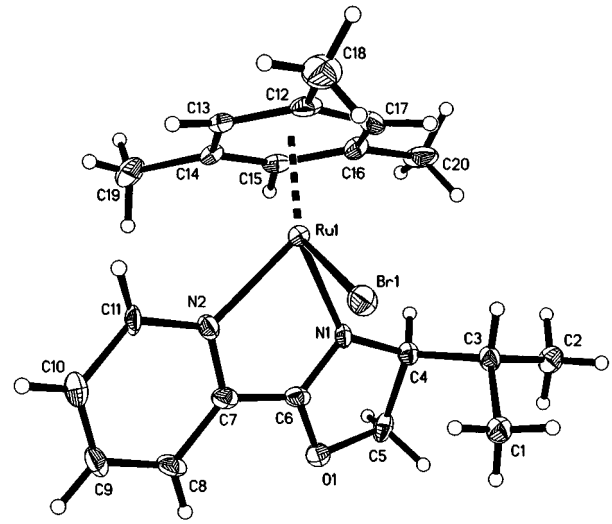


Fig. 1 Molecular structure and atom numbering scheme for the cation of **2b**. Selected bond distances (Å) and angles (°): Ru–N(1) 2.122(11), Ru–N(2) 2.103(10), Ru–Br 2.532(2); N(2)–Ru(1)–N(1) 76.3(4), N(1)–Ru–Br 89.3(3), N(2)–Ru–Br 82.1(3).

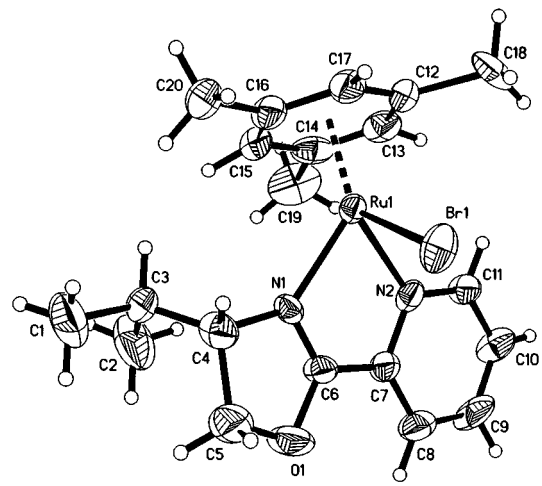


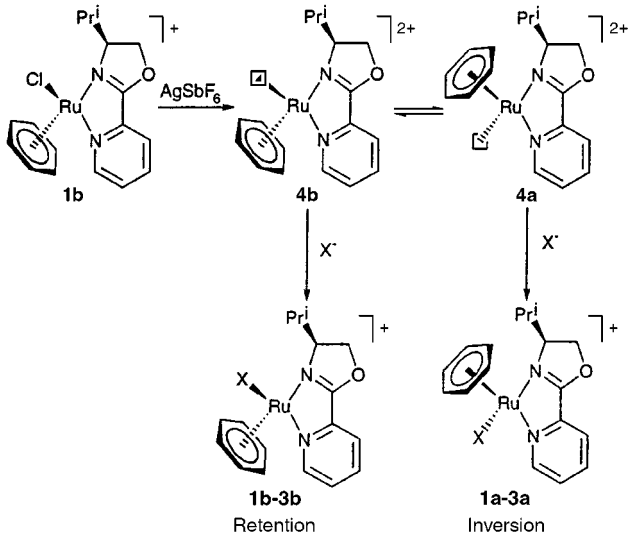
Fig. 2 Molecular structure and atom numbering scheme for the cation of **2a**. Selected bond distances (Å) and angles (°): Ru–N(1) 2.096(10), Ru–N(2) 2.097(13), Ru–Br 2.522(2); N(2)–Ru–N(1) 76.4(5), N(1)–Ru–Br 82.9(3), N(2)–Ru–Br 85.6(4).

than in **2a**. In addition, the N(1)–Ru–Br and N(2)–Ru–Br angles are 89.3(3) and 82.1(3)°, respectively, in **2b**, *i.e.* the oxazoline end of the ligand is inclined slightly away from the bromide to relieve steric congestion between the isopropyl and the bromide; whilst in **2a** the corresponding angles are 82.9(3) and 85.6(4)°, *i.e.* with the pyridine end inclined away from the bromide to minimise steric congestion between the isopropyl and the π-bound arene. The ^{1}H NMR of the crystals showed that **2a** was the major product in the initial mixture.

The chloride (**1**) and iodide (**3**) were formed similarly and the ^{1}H NMR spectra of the crude products show two isomers in a similar 75 : 25 ratio. The ^{1}H NMR spectra, and a crystal structure for **3a**, showed that isomer **a** was preferred in each case. Thus, for **1**, by forming the complex at room temperature we have been able to isolate the kinetic product (**1a**) whilst the preparation in refluxing methanol gave exclusively the thermodynamic isomer (**1b**).[7]

The ^{1}H NMR spectra of crystals of **1a**–**3a** in CD_2Cl_2 showed only the presence of isomer **a**, no trace of isomer **b** was seen even after several days at room temperature. Similarly, the ratios of mixtures of isomers did not change within a few days in CD_2Cl_2 solution. Hence, the configuration at the metal is stable in this solvent. However, in more solvating solvents such as d_4-MeOH or d_6-acetone the isomer ratios were observed to change slowly over a period of days at room temperature or more rapidly at higher temperature, in each case isomer **b** being thermodynamically preferred by at least a ratio of 95 : 5.

Thus, these two-step substitution reactions are unambiguous examples of kinetic control of stereoselectivity with the favoured pathway being a rare case of formal inversion at the metal.[8] We propose the mechanism shown in Scheme 1. Abstraction of halide by Ag^+ provides the aqua/solvent species **4**, epimerisation of which will be much faster than for the halide coordinated species. Species **4a** is expected to react faster since attack of the halide occurs preferentially from the side opposite the oxazoline substituent, *i.e.* the least sterically hindered approach, giving **1a**–**3a** with the isopropyl pointing towards the π-bound arene rather than the halide. The rate of epimerisation of **1**–**3** in methanol is sufficiently slow that it can not account for the amount of isomer **b** formed, *i.e.* the reaction is not forming exclusively isomer **a** followed by epimerisation to isomer **b**. A more precise study of the selectivity, including the effects of different substituents on the oxazoline and the arene and a more detailed kinetic analysis of the reactions will be reported elsewhere.



Scheme 1 (i) □ represents a vacant coordination site or a solvent molecule. (ii) Methyl substituents on the arene have been omitted for clarity.

We thank the University of Leicester (S. A. G.) and EPSRC (A. J. D.) for studentships and Johnson Matthey for a loan of $RuCl_3$.

Notes and references

‡ *Crystal data*: for **2b**: $C_{20}H_{26}BrF_6N_2ORuSb$, M = 727.16, orthorhombic, space group $P2_12_12_1$, a = 8.5892(9), b = 9.5732(14), c = 29.369(3) Å, U = 2414.9(5) Å^3, Z = 4, D_c = 2.000 g cm^{-3}, μ = 3.460 mm^{-1}, F(000) = 1408, graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data collected on a Siemens P4 diffractometer at 190 K. 3782 reflections collected with 2.24 < θ < 27.0°, 3570 unique (R_{int} = 0.0429). An analytical absorption correction was applied. The structure was solved by Patterson methods and refined using full-matrix least squares on F^2 (SHELXL96). Anisotropic displacement parameters used for all atoms, hydrogens included in calculated positions (C–H 0.96 Å), with isotropic displacement parameters set to 1.2 U_{eq}(C) or 1.5 U_{eq}(C) for methyl H atoms. Final R_1 = 0.0534, wR_2 (all data) = 0.1364.

For **2a**: $C_{20}H_{26}BrF_6N_2ORuSb$, M = 727.16, orthorhombic, space group $P2_12_12_1$, a = 7.7030(7), b = 12.0995(17), c = 27.223(2) Å, U = 2537.2(5) Å^3, Z = 4, D_c = 1.904 g cm^{-3}, μ = 3.293 mm^{-1}, F(000) = 1408, graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data collected on a Siemens P4 diffractometer at 200 K. 3234 reflections collected with 1.84 < θ < 25.99°, 3152 unique (R_{int} = 0.0238). A ψ-scan absorption correction was applied. The structure was solved by Patterson methods and refined using full-matrix least squares on F^2 (SHELXL96). Anisotropic displacement parameters used for all atoms, hydrogens included in calculated positions (C–H 0.96 Å), with isotropic displacement parameters set to 1.2 U_{eq}(C) or 1.5 U_{eq}(C) for methyl H atoms. Final R_1 = 0.0579, wR_2 (all data) = 0.1804. CCDC 182/1448. See http://www.rsc.org/suppdata/cc/1999/2331/ for crystallographic files in .cif format.

1 V. I. Sokolov, *Chirality and Optical Activity in Organometallic Compounds*, Gordon and Breach Science Publishers, New York, 1990; H. Brunner, *Angew. Chem., Int. Ed.*, 1999, **38**, 1194.
2 R. Noyori and S. Hashiguchi, *Acc. Chem. Res.*, 1997, **30**, 97; K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya and R. Noyori, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 285; E. P. Kundig, C. M. Saudan and G. Bernardinelli, *Angew. Chem., Int. Ed.*, 1999, **38**, 1220.
3 L. Dadci, H. Elias, U. Frey, A. Hornig, U. Koelle, A. E. Merbach, H. Paulus and J. S. Schneider, *Inorg. Chem.*, 1995, **34**, 306.
4 H. Brunner, R. Oeschey and B. Nuber, *J. Chem. Soc., Dalton Trans.*, 1996, 1499.
5 H. Brunner, R. Oeschey and B. Nuber, *Inorg. Chem.*, 1995, **34**, 3349.
6 N. Gul and J. H. Nelson, *Organometallics*, 1999, **18**, 709; S. Attar, V. J. Catalano and J. H. Nelson, *Organometallics*, 1996, **15**, 2932; H. D. Hansen, K. Maitra and J. H. Nelson, *Inorg. Chem.*, 1999, **38**, 2150; N. Gul and J. H. Nelson, *Polyhedron*, 1999, **18**, 1835.
7 D. L. Davies, J. Fawcett, S. A. Garratt and D. R. Russell, *Chem. Commun.*, 1997, 1351.
8 F. Morandini, G. Consiglio and V. Lucchini, *Organometallics*, 1985, **4**, 1202.

Communication 9/07873H