Synthesis of chiral half-sandwich rhodium oxazoline complexes and their use as asymmetric Diels–Alder catalysts

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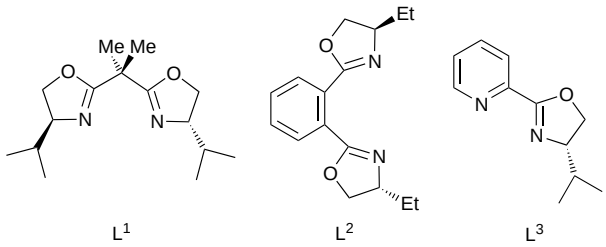
The reaction of $[(\eta\text{-}C_5Me_5)RhCl_2]_2$ with bidentate oxazoline containing ligands provides the cations $[(\eta\text{-}C_5Me_5)RhClL]^+$ 1–3, of which {1, L = 2,2′-isopropylidenebis[4-isopropyl-2-oxazoline] and 3, L = 4-isopropyl-2-(2-pyridyl)-1,3-oxazoline} are structurally characterised by X-ray diffraction; treatment of these with $AgSbF_6$ gives dications which are enantioselective catalysts for the asymmetric Diels–Alder reaction between methacrolein and cyclopentadiene.

Half-sandwich complexes have been extensively used in stoichiometric and catalytic asymmetric synthesis and have therefore attracted much study.[1] Such complexes can be chiral at the ligand and/or the metal. To date much transition metal catalysed asymmetric synthesis has utilised phosphines as chiral ligands, however recently, N-donor ligands have attracted more attention.[2] Oxazolines, in particular, have found extensive use in asymmetric catalysis.[3] For example, bis-oxazolinylpropanes (*cf*. L^1) provide high enantioselectivity in copper catalysed cyclopropanation, aziridination and Diels–Alder reactions[4] whilst pyridyloxazolines (*cf*. L^3) have been used in rhodium catalysed asymmetric hydrosilylation of ketones.[5] However, the use of oxazoline ligands with half-sandwich complexes is much less well studied, being limited to two reports of arene ruthenium complexes.[6,7]

The complexes $[(\eta\text{-}C_5Me_5)RhClL]X$ (X = PF_6, SbF_6) (**1**–**3**; $L^{1–3}$) were prepared in good yield by refluxing the appropriate



ligand with $[(\eta\text{-}C_5Me_5)RhCl_2]_2$ in methanol in the presence of NaX.† In the case of the C_2 symmetric ligands L^1 and L^2, coordination of the ligands is readily apparent in the ^1H NMR spectrum since the C_2 symmetry is lost and only one isomer is possible. For complex **3** containing the unsymmetrical ligand L^3 two diastereomers are possible, however complexation is highly diastereostereoselective, only one diastereomer being observed by ^1H NMR.

The X-ray structures of **1** and **3** were carried out and the structures of the cations with selected bond distances and angles are shown in Figs. 1 and 2 respectively.‡ In each case the rhodium has a pseudo-octahedral geometry with the $\eta\text{-}C_5Me_5$ occupying three *fac* coordination sites. In **1** the Rh–N(1) bond length 2.117(6) Å is slightly shorter than the Rh–N(2) length 2.157(6) Å; possibly the isopropyl on C(12) interacts with the $\eta\text{-}C_5Me_5$ inhibiting a closer approach of N(2). The N(1)–Rh–N(2) chelate bite angle is 84.0(2)°. In **3** the ligand is coordinated such that the isopropyl substituent is on the same side as the chloride rather than the $\eta\text{-}C_5Me_5$ presumably to miminise unfavourable steric interactions. The Rh–N(1) (ox) bond length 2.109(4) is shorter than that of Rh–N(2) (py) 2.142(4) Å, whilst the chelate bite angle N(1)–Rh–N(2) is 76.0(2)° as found for a related arene ruthenium complex with the same ligand.[6] The use of L-valine in the ligand preparation means that the configuration at the chiral carbon is *S* and the structure shows that the rhodium is also *S* [based on the priority

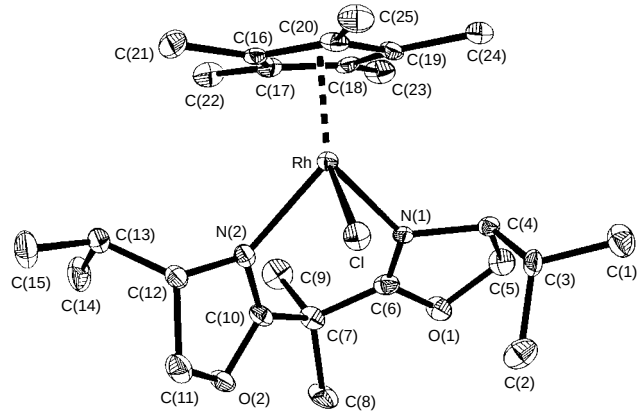


Fig. 1 Molecular structure and atom numbering scheme for the cation of **1**. Selected bond distances (Å) and angles (°): Rh–N(1) 2.117(6), Rh–N(2) 2.157(6), Rh–Cl 2.406(2), N(2)–Ru–N(1) 84.0(2), N(1)–Rh–Cl 90.2(2), N(2)–Rh–Cl 82.1(2).

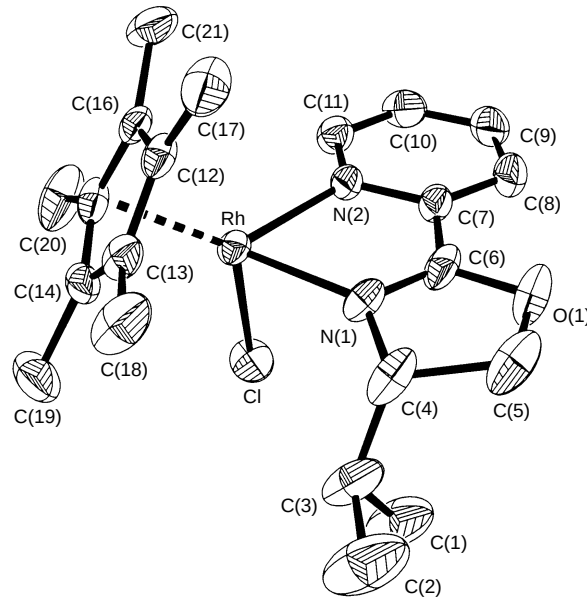
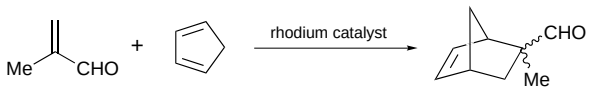


Fig. 2 Molecular structure and atom numbering scheme for the cation of **3**. Selected bond distances (Å) and angles (°): Rh–N(1) 2.109(4), Rh–N(2) 2.142(4), Rh–Cl 2.407(1), N(2)–C(7) 1.345(6), C(7)–C(6) 1.456(8), C(6)–N(1) 1.260(6); N(2)–Rh–N(1) 76.0(2).

Table 1 Enantioselective Diels–Alder reaction of methacrolein with cyclopentadiene in dichloromethane using catalysts prepared from $[(\eta\text{-}C_5Me_5)RhCl(L)]^+$



Entry	Catalyst (mol%)	*T*/°C	*t*/h	Yield (%)	Isomer ratio (*exo*:*endo*)	Ee[a] (%)
1	**1**(5)	room temp.	24	62	94:6	29
2	**2**(5)	room temp.	48	10	90:10	2
3	**3**(1)	room temp.	24	45	94:6	52
4	**3**(2)	room temp.	24	57	94:6	53
5	**3**(2)	0	72	81	95:5	68

[a] Enantiomeric excess of the major *exo* product.

arene > Cl > N (ox) > N (py)].[8] The observation of an NOE effect between the NCH and $\eta\text{-}C_5Me_5$ suggests that this geometry is retained in solution.

Asymmetric catalysis of Diels–Alder reactions mostly with Ti, Al, B or Ln complexes has been reported previously.[9] However, such catalysts are often extremely sensitive to water and may form dimers or oligomers in solution. As a result, characterisation of the actual catalytic species and understanding the mechanism of catalysis and selectivity are particularly difficult. Many of these drawbacks may be overcome with half-sandwich late transition metal Lewis acids. For example, cyclopentadienyl–rhodium[10] and –iron[11] complexes with chiral phosphorus ligands are catalysts for asymmetric Diels–Alder reactions and a related ruthenium complex is a catalyst for the hetero Diels–Alder reaction.[12]

The chloride in **1**–**3** is readily removed with $AgSbF_6$ to form dications. Solutions of these dications in CH_2Cl_2 have been tested as catalysts for the Diels–Alder reaction between methacrolein and cyclopentadiene and the results are shown in Table 1.§ The dication derived from **1** is a reasonable catalyst but gives only modest enantioselectivity (Entry 1) whilst that from **2** shows little or no activity and no enantioselectivity (Entry 2). However, the dication from **3** is a reasonable catalyst even at fairly low catalyst ratio (1 mol%) showing good *exo*:*endo* selectivity with moderate enantioselectivity (Entry 3). Increasing the catalyst ratio gives an increased yield but no increase in ee (Entry 4). However, carrying out the reaction at lower temperature leads to an increase in ee (Entry 5). The absolute configuration of the major *exo* product using **3** as catalyst is consistent with the isopropyl shielding the *Si* face of the coordinated methacrolein leading to attack of cyclopentadiene at the *Re* face as shown in Fig. 3. Coordination of the methacrolein with *Si* face exposed is disfavoured due to steric interactions of the alkene with the $\eta\text{-}C_5Me_5$. The reasons for the difference in catalytic activity of complexes **1**–**3** are not yet clear, though similar reactivity patterns are observed for related arene ruthenium complexes with the same ligands.[6,13]

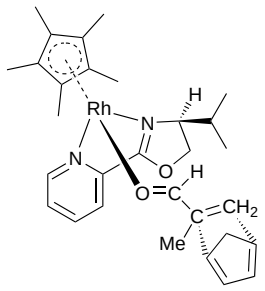


Fig. 3 Model of the transition state

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Footnotes and References

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† *Selected spectroscopic data* for **2**: ^{1}H NMR (250 MHz, $CDCl_3$, 20 °C, $SiMe_4$). δ 0.77 (t, 3 H, *J* 7 Hz, CH_2*Me*), 0.96 (t, 3 H, *J* 7 Hz, CH_2*Me*), 1.29 (s, 15 H, C_5Me_5), 1.60 (m, 2H, C*H*$_2$Me), 1.95 (m, 1 H, C*H*H′Me), 2.30 (m, 1 H, CHH′Me), 4.12 (tt, 1 H, *J* 5, 8.5 Hz, NCH), 4.6 (m, 5 H, 3 ×OCH + 2 × NCH), 7.84 (m, 2 H, aryl), 8.04 (m, 1 H, aryl), 8.16 (m, 1 H, aryl). Satisfactory elemental analysis (C, H, N) obtained for **1**–**3**.

‡ *Crystal data*: for **1**: $C_{25}H_{41}ClF_6N_2O_2RhSb$, M = 775.71, orthorhombic, space group $P2_12_12_1$, a = 13.335(2), b = 13.496(2), c = 17.740(3) Å, U = 3192.7(9) Å^3, Z = 4, D_c = 1.614 g cm^{-3}, μ = 1.505 mm^{-1}, F(000) = 1552, graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Data collected on a Siemens P4 diffractometer at 190 K. 4829 reflections collected with 2.75 < θ < 26.99°, 4619 unique (R_{int} = 0.0173). 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).[14] Anisotropic displacement parameters used for all non-hydrogen atoms, hydrogens included in calculated positions (C–H 0.96 Å), with isotropic displacement parameters set to 1.2 U_{eq}(C). The SbF_6^- anion was found to be disordered, this was modelled with each fluorine atom given equal site occupancy between two different sites. Final R_1 = 0.0743, wR_2 = 0.0784 (all data); Flack parameter, −0.06(3).

For **3**: $C_{21}H_{29}ClF_6N_2OPRh$, M = 608.79, tetragonal, space group $P4_32_12$, a = 12.844(5), c = 30.542(13) Å, U = 5038(3) Å^3, Z = 8, D_c = 1.605 g cm^{-3}, μ = 0.908 mm^{-1}, F(000) = 2464, graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Data collected as above. 7418 Reflections collected with 2.55 < θ < 27.09°, 5507 unique (R_{int} = 0.0256). The structure was solved by Patterson methods and refined using full-matrix least squares on F^2 (SHELXL96).[14] One of the two anions (on special positions) exhibits positional disorder and the F atoms were each assigned fractional occupancy factors. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were generated in their idealised positions (C–H 0.96 Å) and allowed to ride on their respective parent carbon atoms with isotropic displacement parameters set to 1.2 U_{eq}(C). Final R_1 = 0.0731, wR_2 = 0.0801 (all data); Flack parameter, −0.03(4). CCDC 182/648.

§ The catalysis was carried out as described in ref. 6.

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