DALTON
FULL PAPER

Arene ruthenium complexes with pyridyloxazolines: synthesis and applications as asymmetric catalysts for Diels–Alder reactions †

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

Received 9th August 2000, Accepted 13th October 2000
First published as an Advance Article on the web 16th November 2000

Reaction of the dimers $[RuCl_2(arene)]_2$ with pyridyloxazolines (pymox) gave complexes $[RuCl(pymox)(arene)][SbF_6]$ **1**–**12** which have been fully characterised. Using chiral ligands diastereomers are formed, the diastereoselectivity depending on the substituents on the arene and on the oxazoline. The complexes $[RuCl(Me_2\text{-pymox})(mes)][SbF_6]$ **1**, $[RuCl(Ph\text{-pymox})(mes)][SbF_6]$ **3**, $[RuCl(^iPr\text{-pymox})(mes)][SbF_6]$ **5** and $[RuCl(indanyl\text{-pymox})(mes)][SbF_6]$ **12** (mes = mesitylene) have been characterised by X-ray crystallography. Treatment of these cations with $AgSbF_6$ generates dications which in some cases can be isolated as aqua species $[Ru(OH_2)(pymox)(arene)]^{2+}$; these dications are enantioselective catalysts for Diels–Alder reactions of acroleins and dienes; a mechanism is proposed which accounts for the observed enantioselectivity.

Introduction

The stable well defined geometry of half-sandwich complexes means that they are useful substrates for the study of the mechanism of substitution reactions, particularly the stereochemistry of substitution at a chiral metal centre.[1,2] They have also been used successfully as chiral auxillaries in stoichiometric organic synthesis.[3–7] However, their great potential as chiral catalysts has only recently been demonstrated, the best example so far being the transfer hydrogenation of ketones with enantiomeric excesses (ee) of >99% using an arene ruthenium catalyst.[7] In recent years arene ruthenium complexes with chiral ligands have attracted much interest, in particular those with at least one hard donor atom. Examples include amino acids,[8] salicylaldimines,[9,10] pyridyl imines[11,12] anionic pyrrolylimines,[10d–f,13] orthometallated arylethylamines studied by Nelson and co-workers,[14] orthometallated *N*-phenyltriazolinylidene,[15] sulfoxide–carboxylate ligands,[16] bisphosphine monoxides,[17] β-aminoalkyl-phosphines and -phosphites,[18] and we[19] and others[20,21] have reported various oxazoline complexes.

In arene ruthenium complexes with chiral ligands of C_1 symmetry the metal centre is also chiral and two diastereomers are possible. In most cases both diastereomers are formed though in some cases there is very high diastereoselectivity and only one is observed. In the case of amino acidates separation of the diastereomers has not been achieved and crystallisation often gives a 50 : 50 mixture of the two diastereomers. For other ligands a single diastereomer has often been obtained by crystallisation and structurally characterised, however in some of these cases two diastereomers are still observed in solution. In the case of salicylaldimines this is due to relatively easy epimerisation at the metal which is fast on a chemical timescale but slow on the NMR timescale hence, two sets of peaks are observed in the ^1H NMR spectra.[22] Brunner and Zwack have recently shown that the same is true for orthometallated phenylethylamines[23] though previously these were erroneously reported to have a stable metal configuration in solution.[14] We showed that for neutral pyridyl imines one diastereomer could be crystallised selectively and when redissolved the metal centre was stable to epimerisation in dichloromethane for several days.[11] A reduced rate of epimerisation with N,N donor ligands compared to the N,O donor of salicylaldimines has also been noted by others.[12,13]

In this paper we report the diastereoselective synthesis of a number of arene ruthenium pyridyloxazoline complexes and their application as asymmetric Lewis acid catalysts for Diels–Alder reactions. In particular, we describe the effect changing the oxazoline and the arene substituents has on the diastereomer ratio and on the enantioselectivity of the catalysis; some of the work has previously been communicated.[19]

Results and discussion

Synthesis and characterisation of complexes

Reaction of the relevant pyridyloxazoline with the requisite $[RuCl_2(arene)]_2$ in the presence of NaX ($X = PF_6$ or SbF_6) in methanol at reflux gives complexes **1**–**12** in good yields. The complexes were isolated as yellow or orange solids and were characterised by ^1H NMR spectroscopy, mass spectrometry and elemental analysis. The ^1H NMR spectra show downfield shifts for the pyridine and oxazoline protons on coordination particularly for the pyridine 6-H. The FAB mass spectra all show ions corresponding to the cation.

Complex **1** containing an achiral ligand exists as a racemate. The ^1H NMR spectrum shows two singlets for the CMe_2 group and two doublets for the OCH_2 group as expected due to loss of the mirror plane of the ligand on coordination to the ruthenium. The lower symmetry also indicates that interconversion of the enantiomers *i.e.* epimerisation at the metal is slow on the NMR timescale.

Complexes **2**–**12** all contain a chiral ligand and therefore, in principle, may exist as two diastereomers **A** and **B** (Fig. 1). In isomer **A** the oxazoline substituent (R) is oriented towards the arene ring whereas in **B** it is towards the chloride. The size of the oxazoline substituent and of any substituents on the arene is expected to affect the relative ratio of the two diastereomers (see below). For all complexes the diastereomer ratio was determined from the ^1H NMR spectrum of the crude reaction mixture, before recrystallisation, by integration of the arene

† Electronic supplementary information (ESI) available: characterisation data for complexes **13**–**16** and **18**–**24**. See http://www.rsc.org/suppdata/dt/b0/b006530g/

 DOI: 10.1039/b006530g

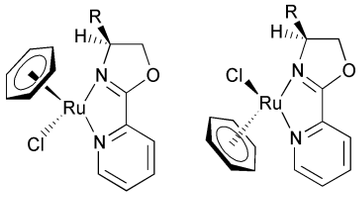
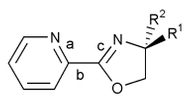
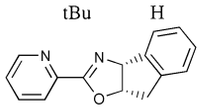


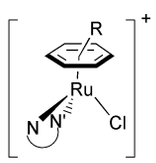
Fig. 1 The two diastereomers of [RuCl(R-pymox)(arene)][SbF_6].



R^1	R^2	abbreviation
Me	Me	Me_2-pymox
H	Et	Et-pymox
Ph	H	Ph-pymox
CH_2Ph	H	Bz-pymox
iPr	H	^{i}Pr-pymox
tBu	H	^{t}Bu-pymox



indanyl-pymox



Complex	Arene	N–N′
1	mes	Me_2-pymox
2	mes	Et-pymox
3	mes	Ph-pymox
4	mes	Bz-pymox
5	mes	^{i}Pr-pymox
6	mes	^{t}Bu-pymox
7	*p*-cymene	^{i}Pr-pymox
8	*p*-cymene	^{t}Bu-pymox
9	benzene	^{t}Pr-pymox
10	benzene	^{t}Bu-pymox
11	C_6Me_6	^{i}Pr-pymox
12	mes	indanyl-pymox

signals (for arene = benzene, mesitylene (mes) and hexamethylbenzene) and/or the pyridine 6-H.

The mesitylene complexes **2** and **4**–**6** were each formed as a single diastereomer; we have previously reported that for **5** this is isomer **B** and the others are presumed to be the same. Complex **3** (R = Ph) was formed as a 5:2 ratio of diastereomers, which after recrystallisation from dichloromethane–diethyl ether gave the major diastereomer exclusively. The ^{1}H NMR spectrum of this isomer displays a triplet at δ 6.10 due to the NCH proton of the oxazoline; the NOESY spectrum shows a cross peak between this signal and those for the mesitylene ring as expected for an isomer **B** structure and the geometry was confirmed by X-ray diffraction (see below). The ^{1}H NMR spectrum showed no trace of the minor isomer even after 1 week in CD_2Cl_2. Separation and evaporation of the mother liquors from the crystallisation yielded a sample heavily enriched in the minor isomer and the isomer ratio did not change over several days. These observations are consistent

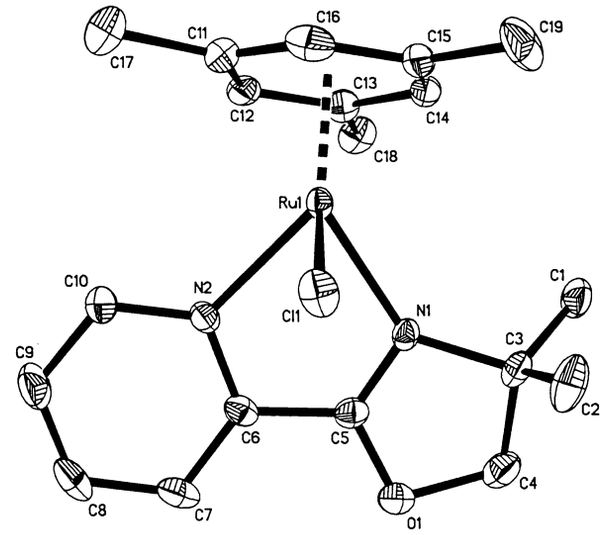


Fig. 2 Molecular structure and atom numbering scheme for the cation of complex **1**; all hydrogen atoms omitted for clarity.

with the chiral ruthenium centre being configurationally stable at room temperature in dichloromethane for several days as observed previously for related pyridylimine complexes.[11,12] This behaviour contrasts with that of the salicylaldimine complexes which epimerise rapidly in dichloromethane and for which the highest equilibrium diastereomer ratio found so far is 86:14.[9,22] When a sample of diastereomerically pure **3** (isomer **B**) is heated in acetone at 40 °C epimerisation does occur very slowly to give an equilibrium ratio of 77:23 (**B**:**A**) after about 40 days.

The high diastereoselectivity in the formation of complexes **2** and **4**–**6** could in principle be due to high stereocontrol in coordination of the ligand, *i.e.* kinetic control, or due to equilibration of the two isomers under the conditions of the synthesis with an equilibrium constant of >50, *i.e.* thermodynamic control. We have shown previously that for **5** the product isolated here (isomer **B**) is indeed the thermodynamically more stable isomer, and that epimerisation of **A** to **B** occurs in refluxing methanol.[24] The high selectivity is therefore at least partly a thermodynamic preference for isomer **B**.

The reason(s) for the lack of diastereoselectivity in the synthesis of complex **3** is (are) not clear. To investigate the effect of the oxazoline and arene substituents on the diastereomer ratio we synthesized complexes **7**–**11**. Complexes **7**, **9** and **11** all contain an oxazoline with an isopropyl substituent. The *p*-cymene and benzene complexes, **7** and **9** respectively, are formed as 50:50 mixtures of diastereomers however the corresponding mesitylene and hexamethylbenzene complexes, **5** and **11** respectively, are each formed as a single diastereomer. This implies that the number of substituents on the arene is more important than their size. However, when the oxazoline substituent is ^{t}Bu, complexes **6**, **8**, and **10**, only one isomer is isolated independent of the susbtitution pattern of the arene.

In order to probe further the role of steric interactions in controlling the diastereoselectivity we have synthesized complex **12** containing a fused ring substituent and have determined the structures of complexes **1**, **3** (major isomer), **5** and **12** by X-ray diffraction. The molecular strucutres of the cations are shown in Figs. 2–5 with selected bond distances and angles in Table 1. Complex **3** required a change of counter ion to $[BPh_4]^-$ to provide crystals suitable for X-ray diffraction, whilst **5** was determined as the PF_6 salt. Complexes **3**, **5** and **12** all have an isomer **B** structure with the oxazolinyl substituent on the same side as the chloride and away from the arene ring. The immediate coordination sphere of the metal is similar in all the complexes. Thus, the Ru–N_{ox}, Ru–N_{py}, and Ru–Cl distances and N–Ru–N angles are very similar for the four complexes; the

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1**, **3**, **5** and **12**

	1[a]	**3**	**5**	**12**
$Ru–N_{ox}$	2.128(5)	2.105(5)	2.118(4)	2.103(5)
$Ru–N_{py}$	2.125(5)	2.104(5)	2.117(4)	2.126(5)
Ru–Cl	2.397(2)	2.403(2)	2.402(2)	2.393(2)
a[b]	1.354(8)	1.335(8)	1.351(7)	1.346(8)
b[b]	1.446(9)	1.454(8)	1.449(8)	1.435(9)
c[b]	1.279(8)	1.285(7)	1.280(7)	1.285(8)
N–Ru–N	76.4(2)	76.4(2)	76.4(2)	76.5(2)
$N_{ox}–Ru–Cl$	84.6(2)	87.9(1)	88.5(1)	87.5(1)
$N_{py}–Ru–Cl$	82.8(2)	80.8(1)	82.6(1)	81.1(2)

[a] The bond lengths and angles are averages for the two independent molecules in the uinit cell. [b] The bonds *a*, *b* and *c* are defined in the diagram of the ligands.

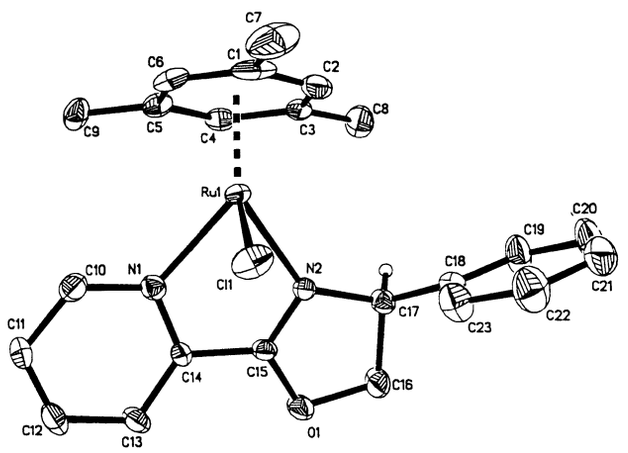


Fig. 3 Molecular structure and atom numbering scheme for the cation of complex **3**; all hydrogen atoms, except that on the chiral carbon atom, omitted for clarity.

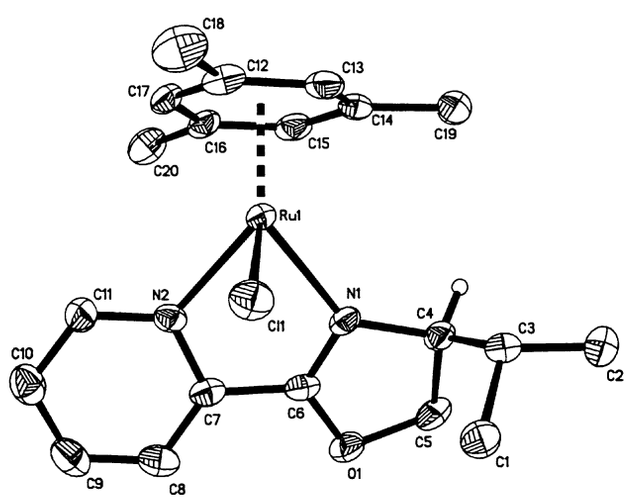


Fig. 4 Molecular structure and atom numbering scheme for the cation of complex **5**; details as in Fig. 3.

$Ru–N_{ox}$ and $Ru–N_{py}$ bond lengths being the same within each complex except for **12** in which the $Ru–N_{ox}$ distance 2.103(5) Å, is slightly shorter than $Ru–N_{py}$, 2.126(5) Å. The only significant differences in the metal coordination sphere are the $N_{ox}–Ru–Cl$ and $N_{py}–Ru–Cl$ angles. For complexes **3**, **5** and **12** the $N_{ox}–Ru–Cl$ angles range from 87.5(1) to 88.5(1)° and the $N_{py}–Ru–Cl$ ones from 80.8(1) to 82.6(1)° with a difference between the two of at least 5.9° in each complex. Thus the oxazoline end of the ligand appears to tilt away from the chloride, possibly to relieve

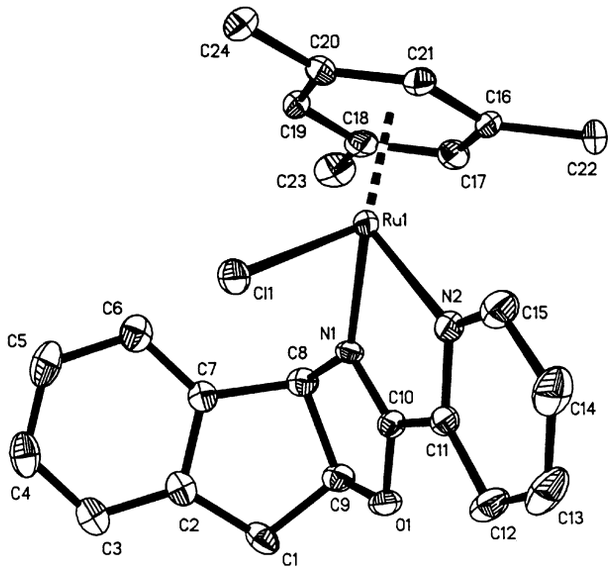


Fig. 5 Molecular structure and atom numbering scheme for the cation of complex **12**; all hydrogen atoms omitted for clarity.

steric conflict with the oxazoline substituent. In **1** the $N_{ox}–Ru–Cl$ and $N_{py}–Ru–Cl$ angles are more nearly the same at 84.6(2) and 82.8(2)° respectively. In this case, increasing the $N_{ox}–Ru–Cl$ angle to relieve steric interactions between the methyl and chloride would simultaneously increase interactions between the other methyl and the arene. We have reported that for the bromide analogue of complex **5** the $N_{ox}–Ru–Cl$ angle of 89.3(3)° is larger than the $N_{py}–Ru–Cl$ angle of 82.1(3)° in isomer **B**, whilst the reverse is true [$N_{py}–Ru–Cl$ 85.6(4) and $N_{ox}–Ru–Cl$ 82.9(3)°] in isomer **A**.[24]

The similarity of the structure of the major isomer of complex **3** with those of **5** and **12** suggests that the lack of diastereoselectivity in formation of **3** is not a consequence of unfavourable interactions in the major isomer but rather a relative increase in stability of the minor isomer. It is possible that in the minor isomer (**A**) the phenyl substituent is able to orient itself pseudo-parallel to the mesitylene ring thus relieving unfavourable steric interactions in this isomer. In contrast, in **2** and **4**–**6** the oxazoline substituent has bulk in three dimensions and so cannot avoid some interaction with the mesitylene ring. It is notable that in **12** the phenyl ring C(2)–C(7) is oriented almost perpendicular to the plane of the mesitylene ring. This orientation is fixed due to the fused ring connection with the oxazoline. It would presumably also make isomer **A** less stable and is not observed in this case.

The circular dichroism spectra of some of the complexes have been measured to establish whether it is a reliable indicator of the configuration of the metal. The spectra for selected complexes are shown in Fig. 6. In complex **5** the ^{i}Pr-pymox ligand has *S* configuration at the carbon (S_C) and the crystal structure shows the configuration at ruthenium is also *S i.e.* the S_CS_{Ru} enantiomer. If complex **5** is synthesized using the R_C ligand the R_CR_{Ru} isomer is formed as expected and the CD spectrum is the mirror image of the S_CS_{Ru} isomer (Fig. 6a). The ethyl substituted complex **2** was made with the *R*-configured ligand and isomer **B** is therefore R_CR_{Ru} and the CD spectrum (Fig. 6b) is very similar to that of the R_CR_{Ru} enantiomer of **5**. The phenyl- and benzyl-substituted complexes **3** and **4** respectively each contain an S_C ligand and their CD spectra (pure major isomer for **3**) are very similar to that of the S_CS_{Ru} isomer of **5** (Fig. 6b). The "free" ligands show very little absorption in the CD spectra in the range 230–600 nm thus these absorptions are arising from the metal environment. We conclude that the signs of the absorptions between 230 and 600 nm in the CD spectra are a reasonable guide to the configuration at the metal

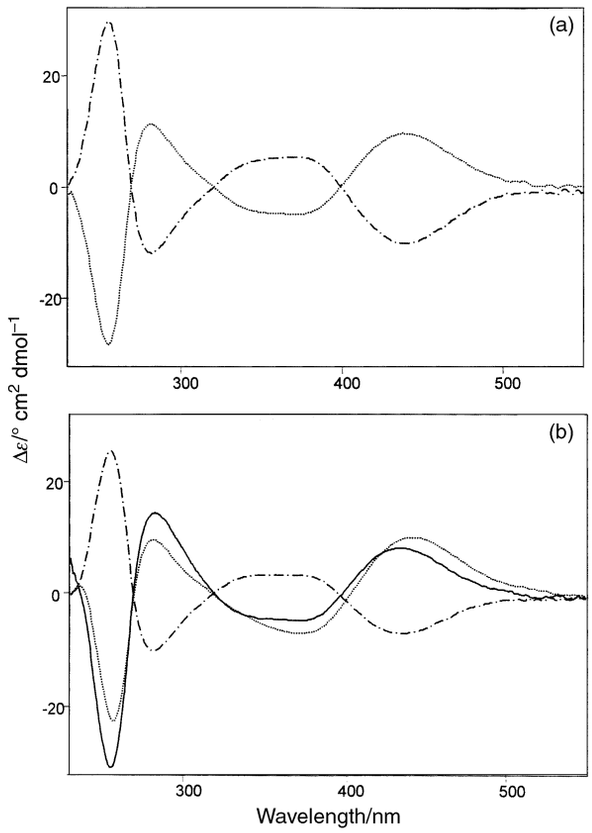


Fig. 6 CD spectra of complexes **2**, **3**, **4** and **5** (CH_2Cl_2, 2 mg cm^{-3}, d = 1 mm). (a) (·····) ([RuCl(S_C-^{i}Pr-pymox)(mes)]SbF_6 **5**, (-··-) [RuCl(R_C-^{i}Pr-pymox)(mes)]SbF_6 **5**; (b) (-··-) [RuCl(R_C-Et-pymox)(mes)]SbF_6 **2**, (·····) [RuCl(S_C-Ph-pymox)(mes)]SbF_6 **3**, (———) [RuCl(S_C-Bz-pymox)(mes)]SbF_6 **4**.

for these $[RuCl(pymox)(arene)]^+$ cations. The generality of this observation, and its extension to other oxazoline-containing ligands and ancillary ligands other than chloride will be reported in future publications.

In order to use the half-sandwich oxazoline complexes as catalysts, it is necessary to remove the chloride ligand. Aqua complexes $[Ru(OH_2)(L)(arene)][SbF_6]_2$ **13**–**24** were synthesized from their chloride precursors using $AgSbF_6$ in CH_2Cl_2–acetone (7:1). The water molecule may come partly from traces of water in the acetone and/or may be absorbed during the work-up which is usually carried out in air. Pure complexes could be isolated by filtration of the crude reaction mixtures through Celite, to remove the AgCl by-product; however, many of the dications were somewhat hygroscopic and recrystallisations often gave oily products, hence microanalyses were not obtained in all cases.

Complexes **13**–**24** are all insoluble in $CHCl_3$, sparingly soluble in CH_2Cl_2, but very soluble in polar solvents such as acetone and MeOH. The ^{1}H NMR spectra are very similar to those of the chloride precursors except for additional equilibria in coordinating solvents (eqn. 1). The ^{1}H NMR spectrum

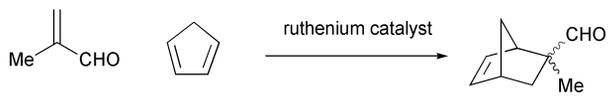
$$[Ru(OH_2)(pymox)(arene)][SbF_6]_2 \underset{H_2O}{\overset{acetone}{\rightleftharpoons}} [Ru(acetone)(pymox)(arene)][SbF_6]_2 \quad (1)$$

of **13** in d_6-acetone surprisingly showed a mixture of two similar species, the ratio of which depended on the amount of free water in solution. Thus, incremental addition of water increased the ratio and eventually led to disappearance of the minor set of peaks. The major species showed signals due to the arene and pyridine fragments, shifted to higher frequency compared to those of **1** by up to 0.35 ppm (py 6-H) as expected for a dication, two singlets for the CMe_2 group and two doublets for the OCH_2 group, consistent with epimerisation being slow on the NMR timescale, with a singlet (relative integration 2H) at δ 6.5 assigned to the coordinated water and a singlet at δ 2.9 due to free water. The observation of separate signals for free and coordinated water indicates that exchange of water (even proton exchange) is relatively slow compared with the NMR timescale. Thus, the major species was assigned as an aqua dication. The minor species exhibited sharp signals due to the arene and pyridine ring signals, but very broad resonances at δ 1.8 (CMe_2) and 4.9 (OCH_2) clearly indicating that epimerisation at the metal was occurring at a rate comparable to the NMR timescale. On cooling the sample to 253 K, the broad signal at δ 1.8 resolved into two 3H singlets (δ 1.75 and 2.15) and the broad peak at δ 4.9 resolved into two 1H doublets (δ 4.89 and 4.96). Thus, the minor species was assigned as an acetone-coordinated complex with epimerisation at the metal being considerably faster with acetone coordinated than with water. Thus, in acetone the equilibrium (1) has a significant proportion of species with solvent coordinated in place of water. To shift the equilibria to the left and hence simplify the spectra, the ^{1}H NMR spectra of the other species were run in CD_2Cl_2–d_6-acetone (10:1) where possible. The ^{1}H NMR spectrum of **13** gives only one set of signals with a slightly broad 2H singlet at δ 5.5 assigned to coordinated H_2O, and a broad singlet at δ 1.8 due to free water, with no signals due to an acetone coordinated complex being observed.

The ^{1}H NMR spectra of the chiral complexes **14**–**24** reveal that in all cases in which the chloride precursor was prepared as a single diastereomer the aqua complex also exists as a single diastereomer. All the spectra also show separate signals due to coordinated and free water, thus water exchange is slow relative to the NMR timescale. Interestingly, complex **15** (R = Ph) exists as only one diastereomer as determined from the ^{1}H NMR spectrum, when synthesized either from pure isomer **B** or the 5:2 (**B**:**A**) mixture of diastereomers of **3**. This suggests that the diastereomers of **15** can interconvert on a chemical timescale and that there is a strong thermodynamic preference for one diasteromer. The only ruthenium aqua compounds that appear as mixtures of diastereomers are the benzene complex **21** and the *p*-cymene complex **19**. These complexes are poorly soluble in CD_2Cl_2 and the ^{1}H NMR spectra were only obtained in d_6-acetone. In the initial spectrum of **21** four signals were observed due to η^6-C_6H_6 groups (δ 6.48, 6.54, 6.59 and 6.64) in a ratio 1:9:1.3:11.4. Addition of an excess of water to the sample dramatically reduced the integration of the two higher frequency signals, which are thus assigned to diastereomeric acetone-coordinated complexes. The ratio of the two remaining singlets remained unchanged throughout and the equilibrium ratio of isomers for the aqua-complex is deduced as 9:1. In addition, singlets due to coordinated H_2O in the diastereomers can be observed, again in a 9:1 ratio. This isomer ratio is considerably higher than that found for the chloro-bound precursor (1:1). Similar features are observed in the NMR spectra of **19** with the diastereomer ratio again deduced as 9:1.

The ^{1}H NMR spectra of complexes **14**–**24** in pure d_6-acetone contain a second minor set of signals which are assigned to acetone-coordinated complexes (eqn. 1). Addition of small quantities of water to the samples leads to the disappearance of the minor species, as expected, due to displacement of acetone by water. In many spectra an extra signal is observed at δ 6–7, up to 0.1 ppm to *high* frequency of the coordinated H_2O signal. Addition of an excess of water leads to the disappearance of the higher frequency signal, whilst with excess of D_2O both singlets disappear. Addition of *small* quantities of D_2O (*i.e.* several equivalents) to the NMR sample results in a proportional increase in the higher frequency water signal, with an overall decrease in the integration of the pair of singlets, with respect to the other signals. The same effect is observed with **13** so can not be attributed to diastereomeric complexes. We thus assign this extra peak to coordinated HOD, a rare example of a

Table 2 Enantiomeric Diels–Alder reaction of methacrolein with cyclopentadiene in dichloromethane catalysed by [RuCl(pymox)(arene)][SbF_6] after treatment with $AgSbF_6$



Entry	Catalyst precursor	% Catalyst	*T*/°C	*t*/h	Yield (%)	*exo*:*endo*	ee (%) (abs. config.)
1	**2**[a]	2	0	4	61	95:5	54 (*R*)[a]
2	**3**	2	0	7	30	94:6	58 (*S*)
3	**4**	2	0	6	31	95:5	70 (*S*)
4	**5**	2	0	4	72	95:5	75 (*S*)
5	**6**	2	0	5	94	96:4	83 (*S*)
6	**12**[a]	2	0	72	23	93:7	6 (*S*)[a]
7	**5**	0.5	rt	0.25	95	95:5	70 (*S*)
8	**5**	1	rt	0.2	95	95:5	70 (*S*)
9	**5**	2	rt	0.3	95	95:5	71 (*S*)
10	**5**	5	rt	0.5	95	94:6	72 (*S*)
11	**5**	5	−20	72	90	96:4	81 (*S*)
12	**7**	2	0	24	91	93:7	45 (*S*)
13	**9**	2	0	24	73	90:10	18 (*S*)
14	**11**	2	0	24	93	94:6	66 (*S*)

[a] The R_C-configured ligand was used.

high frequency deuterium isotope shift. Such effects have been observed before, often in systems where hydrogen bonding occurs.[25]

Catalysis

There is a need for new chiral catalysts for use in the synthesis of enantiopure chemicals particularly for the pharmaceutical industry. Chiral Lewis acids are particularly important in catalysing C–C bond forming processes. However, traditional Lewis acids, complexes of boron, aluminium and titanium, have a number of disadvantages, *viz.* sensitivity to water, strong binding of carbonyls which can lead to product inhibition and low turnover rates. Furthermore, in many cases the catalysts have been prepared *in situ* and the actual catalytic species has only been inferred. A clear picture of the mechanism of reaction at a molecular level is necessary to understand the basis of enantioselectivity and hence allow rational development of new catalysts. It is recognised[26] that low or medium oxidation state complexes of middle to late transition metals, *e.g.* half-sandwich arene ruthenium complexes, offer many advantages. Such complexes are often well characterised, and air- and moisture-stable, potentially allowing greater understanding of the molecular basis of the enantioselectivity (rational catalyst design). Kundig *et al*. have recently reported a chiral cyclopentadienyl ruthenium complex which is an enantioselective catalyst of Diels–Alder reactions and can also be recycled.[27] Arene ruthenium complexes of bisphosphine monoxides[17b] or pyridyl imines[12] can also catalyse such reactions though with lower enantioselectivity.

The dications **13**–**24**, described above are good Lewis acids and can catalyse the Diels–Alder reaction of methacrolein (methacrylaldehyde) with dienes. Reactions can be run on isolated samples of **13**–**24**, or using the solution obtained directly from treatment of [RuCl(pymox)(arene)][SbF_6] **1**–**12** with $AgSbF_6$ after filtration to remove the AgCl, similar catalytic results being observed in either case. The results (Table 2) will be described in terms of the chloride precursor complexes **1**–**12**. All the complexes provide good *exo*:*endo* selectivity. Complexes **2**–**6** show modest to good enantioselectivity (entries 1–5) with the enantiomeric excess increasing as the size of the oxazoline substituent increases to a maximum of 83% for R = ^{t}Bu. The phenyl (**3**) and benzyl (**4**) complexes give lower yields due to slower rates of reaction, though particularly for benzyl the ee is still good. The reasons for the slower rate with these substituents is not known. Using the indanyl-pymox (entry 6) the

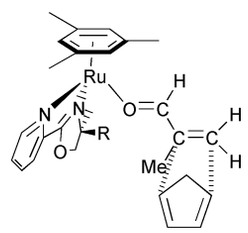


Fig. 7 Proposed transition state showing approach of cyclopentadiene.

enantiomeric excess is small, however the rate of reaction is much slower in this case, possibly due in part to a low solubility, which may allow competition by the racemic thermal reaction. The effects of catalyst loading (entries 7–10) and temperature (entries 4 and 11) were investigated using catalyst **5**. The catalyst loading has little effect on rate or enantioselectivity between 0.5 and 5 mol% though lowering the temperature to −20 °C did lead to an increase in enantiomeric excess.

Complexes **5**, **7**, **9** and **11** allow consideration of the effect of substituents on the arene ring (entries 4 and 11–13). Thus, when the oxazoline substituent is ^{i}Pr the enantioselectivity reaches a peak when the arene is mesitylene (ee 71%). The less substituted benzene complex **9** gives a much lower ee of 18% as expected, whilst the hexamethylbenzene complex **11** only gives 66%. It is notable that Noyori and Hashiguchi found similar effects on enantioselectivity by altering the arene substituents in transfer hydrogenation of ketones.[7] The lower selectivity for the benzene and *p*-cymene complexes is consistent with the presence of some of the other diastereomer (isomer **A**), since in that case the oxazoline substituent is on the opposite side to the methacrolein and hence would not be expected to influence the enantioselectivity significantly, *i.e.* isomer **A** is expected to give a racemic product.

Using S_C-ligands the major product was identified as (1*R*,2S,4*R*)-2-methylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde, by comparison of the sign of the optical rotation and the GC behaviour of the acetal formed from (2*R*,4*R*)-pentanediol with literature values.[28] The absolute configuration of the major *exo* product using complex **5** 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. 7. Further evidence in support of this mechanism has come from studying the coordination of methacrolein. Thus, [Ru(CH_2CMeCHO)(^{i}Pr-pymox)(mes)][SbF_6] **25** was formed

Table 3 Enantioselective Diels–Alder reactions catalysed by [RuCl(*R*-pymox)(mes)][SbF_6] (R = ^{i}Pr, **5** or ^{t}Bu, **6**) after treatment with $AgSbF_6$ using 2 mol% catalyst in dichloromethane

Diene	Dienophile	Catalyst precursor	Temperature	*t*/h	Isomer ratio	ee (%)
Isoprene	Methacrolein	**5**	rt	13	>98% 1,4	90
DMBD	Methacrolein	**5**	rt	5		74
DMBD	Methacrolein	**6**	rt	13		84
Cyclopentadiene	Acrolein	**5**	0	2	*exo*:*endo* 1:2	36
Cyclopentadiene	Acrolein	**6**	0	2	*exo*:*endo* 1:2	46
DMBD	Acrolein	**5**	rt	24		50

The absolute configuration of the products was not measured. acrolein = CH_2CHCHO.

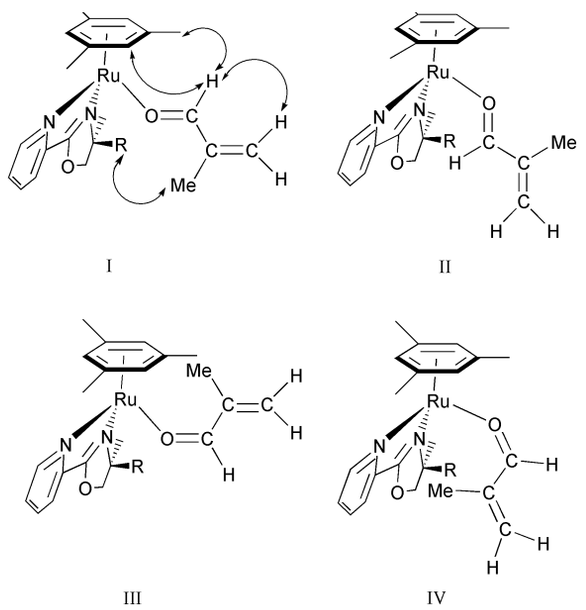


Fig. 8 Possible orientations of coordinated methacrolein and observed NOEs.

by treatment of **5** with $AgSbF_6$ and methacrolein in CD_2Cl_2, in the presence of molecular sieves to remove water. The ^{1}H NMR spectrum showed signals due to complex **25** as well as a small amount of the aqua complex **17** as well as signals due to free methacrolein and a small amount of free water. The coordinated aldehyde proton is observed at δ 9.10, a shift of 0.44 ppm upfield on coordination. This is much larger than the 0.02 ppm shift reported for aldehyde coordination to an areneruthenium bisphosphine monoxide complex.[17] Assuming that the methacrolein lies in a plane roughly perpendicular to the pymox ligand four distinct orientations are possible (Fig. 8). The aldehyde can coordinate through the lone pair *syn* to the aldehyde proton (**I** and **II**) or the lone pair *anti* (**III** and **IV**). In each case there are two rotamers corresponding to rotation about the Ru–O bond. The orientation of the methacrolein was probed using NOESY spectroscopy; the observed cross peaks are shown in Fig. 8 (Structure **I**). For the coordinated methacrolein cross peaks are observed between the aldehyde proton and one H of the terminal CH_2 group, consistent with an *S-trans* arrangement.[29] Cross peaks were also observed between the coordinated aldehyde proton and the methyl and arene protons on the mesitylene ring and between the methyl of the methacrolein and one of the methyls of the isopropyl. Notably there are no cross peaks between the methyl of the methacrolein and any of the mesitylene signals. Of the four possible orientations **I** to **IV** these observations are only consistent with **I**. A similar orientation was found in solution and in the solid state by Kundig *et al.*[27] in a cyclopentadienyl ruthenium complex, whereas an orientation similar to **II** was observed in the solid state by Carmona *et al.*[21] in a rhodium complex, though both these cases involved at least one coordinated phosphine. In addition to the NOE cross peaks, chemical exchange cross peaks were observed between free and coordinated methacrolein so this exchange is occurring within the timescale of the NOESY experiment.

Complexes **5** and **6** were also screened as catalyst precursors for Diels–Alder reactions with other substrates (Table 3). The reactions were carried out in an NMR tube and gave yields of >95% determined by integration. The reactions of methacrolein with isoprene or 2,3-dimethylbutadiene (DMBD) both proceeded with high enantioselectivity, catalysed by **5** and **6**. Using **5** as catalyst the isoprene adduct was obtained as the 1,4-regioisomer (>98%), with an ee of 90%, whilst the DMBD adduct was obtained in 74% ee. Using **6** as catalyst for the DMBD reaction an ee of 84% was obtained under the same conditions. Using other Lewis acid catalysts (*e.g.* alkoxyboranes[30]) the DMBD–methacrolein adduct is obtained in higher ee than the corresponding isoprene adduct; it is not clear why complex **5** gives a smaller ee with DMBD. With cyclohexadiene no reaction with methacrolein was observed using **5** as catalyst under the conditions described above, possibly due to steric factors.

Complexes **5** and **6** were also used as catalysts (2 mol%) for the Diels–Alder reactions of cyclopentadiene or DMBD with acrolein (Table 3). The reaction of acrolein with cyclopentadiene is faster than with methacrolein, reaching completion after two hours at 0 °C with catalysts **5** and **6**. The selectivity, however, is considerably reduced with acrolein; the *exo*:*endo* ratios obtained were all 1:2, with the highest ee obtained (for major *endo* product) being 46%. The reaction of acrolein with DMBD catalysed by **5** proceeds more slowly than that with cyclopentadiene, but gives higher enantioselectivity (ee 50%). Since the size of the α-substituent of the dienophile affects the selectivity, the reaction of α-bromoacrolein with cyclopentadiene was studied; this reaction proceeds with high enantioselectivity with a number of chiral catalysts.[31,32] Surprisingly, **5** was found to be a poor catalyst for this reaction; only a 20% yield of product (*exo*:*endo* ratio 80:20) was obtained after 90 min at 0 °C consistent with the uncatalysed thermal reaction. It is possible that coordination of bromoacrolein to the Ru/pymox complexes is disfavoured on steric grounds or that bromide abstraction from the product occurs causing deactivation of the catalyst.[27] We have shown that other ruthenium oxazoline complexes are capable of catalysing reactions using bromoacrolein and these will be reported elsewhere.

In conclusion, we have shown that by suitable choice of substituents on the arene and/or the oxazoline it is possible to synthesize complexes [RuCl(pymox)(arene)][SbF_6] diastereomerically pure. The configuration at ruthenium of such cations is stable in dichloromethane at room temperature. Abstraction of the chloride with $AgSbF_6$ gives dications which can catalyse Diels–Alder reactions with high enantioselectivity in some

cases. Indeed the enantioselectivity is the highest observed so far using arene ruthenium complexes as catalysts for Diels–Alder reactions. The structure of the coordinated methacrolein has been probed by ^{1}H NMR spectroscopy and this has led to formulation of a mechanism to account for the observed enantioselectivity.

Experimental

Light petroleum (bp 40–50 °C) and diethyl ether were dried by refluxing over purple sodium–benzophenone under nitrogen, whilst dichloromethane was purified by refluxing over calcium hydride and acetone from calcium sulfate. 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. ^{1}H NMR spectra were obtained using Bruker 250, 300 and 400 MHz spectrometers in CD_2Cl_2 unless stated otherwise, chemical shifts being recorded in ppm (referenced to tetramethylsilane or residual protons in the NMR solvent). FAB mass spectra were obtained on a Kratos concept mass spectrometer using a 3-nitrobenzyl alcohol matrix. Microanalyses were performed by Butterworth laboratories Ltd., Middlesex. Circular dichroism spectra were run on a JASCO J-715 spectropolarimeter, polarimetric measurements on a Perkin-Elmer 341 instrument at ambient temperature at 589 nm, concentration in g per 100 ml solution.

The ligands R^{1}R^2-pymox (R^1 = R^2 = Me; R^1 = H, R^2 = Et, ^{i}Pr, ^{t}Bu, Ph or Bn) were prepared by literature procedures[33,34] from the relevant aminoalcohols which in turn were prepared by reduction of the amino acids[35] (99% optical purity), except for 2-amino-2-methyl-1-propanol and (1*R*, 2*S*)-*cis*-1-amino-2-indanol (99% optical purity) which was obtained from Aldrich. The complexes $[RuCl_2(arene)]_2$ (arene = C_6H_6, *p*-cymene, mesitylene, or C_6Me_6)[36,37] were prepared using literature procedures.

Preparations

Indanyl-pymox. This was prepared by analogy with the other pymox ligands. A mixture of pyridinecarboxyimidate {C_5H_4N[C(=NH)OMe]-2}) (273 mg, 2.0 mmol), (1*R*,2*S*)-1-amino-2-indanol (300 mg, 2.0 mmol), concentrated HCl(aq) (1 drop) and $CHCl_3$ (1 cm^3) was stirred overnight at 60 °C. The resulting yellow paste was purged with N_2, to remove any remaining MeOH and ammonia (by-products of the reaction) and then evaporated *in vacuo*. The crude product was chromatographed on silica, with CH_2Cl_2–MeOH (95 : 5) as eluent. Evaporation of the fore-run gave an oily product; washing with hexane afforded an off-white solid, Yield = 376 mg (79%). ^{1}H NMR: δ 3.50 (m, 2H, CH_2Ar), 5.58 (ddd, *J* 10.5, 8, 2.5, OCH), 5.81 (d, 1H, *J* 8, NCH), 7.27 (m, 3H, Ar H), 7.35 (ddd, 1H, *J* 8, 5, 1, py 5-H), 7.59 (dd, 1H, *J* 5.5, 3.5, Ar H), 7.73 (dt, 1H, *J* 2, 8, py 4-H), 8.04 (d, 1H, *J* 8, py 3-H) and 8.68 (dd, 1H, *J* 5, 1 Hz, py 6-H). MS (FAB$^+$): *m*/*z* 237 (MH$^+$).

[RuCl(pymox)(arene)][SbF$_6$] 1–12. A solution of the ligand (2.1 equivalents) and $NaSbF_6$ (2.1 equivalents) in MeOH (10 cm^3) was added to $[RuCl_2(arene)]_2$ (1 equivalent) and the resulting suspension heated to reflux for one hour. An orange-brown solution was obtained, which was then evaporated and the crude residue dissolved in CH_2Cl_2. Filtration through Celite (to remove NaCl and any black decomposition product) gave a red-orange solution and evaporation of the solvent afforded the crude complex. The diastereomer ratio was measured at this stage and the complexes could be recrystallised from CH_2Cl_2–diethyl ether. The scale and yields for individual complexes are shown below.

[RuCl(Me$_2$-pymox)(mes)][SbF$_6$] ***1***. Complex **1** was prepared from $[RuCl_2(mes)]_2$ (80 mg, 0.137 mmol), Me$_2$-pymox (53 mg, 0.30 mmol) and $NaSbF_6$ (75 mg, 0.29 mmol), in 169 mg yield, 92%. mp 265 °C. Calc. for $C_{19}H_{24}ClF_6N_2ORuSb$: C, 34.13; H, 3.62; N, 4.19. Found: C, 34.45; H, 3.54; N, 4.05%. ^{1}H NMR: δ 1.42 (s, 3H, CMe$_2$), 1.73 (s, 3H, CMe$_2$), 2.25 (s, 9H, C_6Me_3), 4.44 (d, 1H, *J* 9, OCH) 4.61 (d, 1H, *J* 9, OCH), 5.70 (s, 3H, $C_6H_3Me_3$), 7.72 (m, 1H, py 5-H), 7.83 (d, 1H, *J* 8, py 3-H), 8.05 (t, 1H, *J* 8, py 4-H) and 9.05 (d, 1H, *J* 5 Hz, py 6-H). MS (FAB$^+$): *m*/*z* 433, [M]$^+$.

[RuCl(Et-pymox)(mes)]SbF$_6$ ***2***. Complex **2** was prepared from $[RuCl_2(mes)]_2$ (80 mg, 0.137 mmol), Et-pymox (53 mg, 0.30 mmol) and $NaSbF_6$ (75 mg, 0.29 mmol), in 172 mg yield, 94%. Calc. for $C_{19}H_{24}ClF_6N_2ORuSb$: C, 34.13; H, 3.62; N, 4.19. Found: C, 34.82; H, 3.66; N, 4.47%. ^{1}H NMR: δ 0.87 (t, 3H, *J* 7.5, CH$_2$*Me*), 1.47 (m, 1H, C*H*Me), 1.99 (m, 1H, C*H*Me), 2.19 (s, 9H, C_6Me_3), 4.76 (dd, 1H, *J* 8.5, 5.5, OCH), 4.93 (m, 1H, NCH), 5.05 (t, 1H, *J* 8.5, OCH), 5.54 (s, 3H, $C_6H_3Me_3$), 7.81 (m, 1H, py 5-H), 7.91 (d, 1H, *J* 7, py H-3), 8.19 (td, 1H, *J* 7, 1, py H-4) and 9.36 (d, 1H, *J* 5 Hz, py 6-H). MS (FAB$^+$): *m*/*z* 433, [M]$^+$.

[RuCl(Ph-pymox)(mes)][SbF$_6$] ***3***. Complex **3** was prepared from $[RuCl_2(mes)]_2$ (70 mg, 0.12 mmol), Ph-pymox (59 mg, 0.26 mmol) and $NaSbF_6$ (65 mg, 0.25 mmol) in 163 mg yield, 95%. The X-ray structure determination was carried out on the BPh_4 salt. Calc. for $C_{23}H_{24}ClF_6N_2ORuSb$: C, 35.98; H, 3.27; N, 3.50. Found: C, 35.67; H, 2.97; N, 3.53%. ^{1}H NMR: major isomer δ 2.11 (s, 9H, C_6Me_3), 4.55 (dd, 1H, *J* 11, 8.5, OCH), 5.49 (t, 1H, *J* 11, 8.5, OCH), 6.10 (t, 1H, *J* 11, NCH), 5.22 (s, 3H, $C_6H_3Me_3$), 7.44 (m, 3H, Ph), 7.58 (m, 2H, Ph), 7.78 (m, 1H, py 5-H), 7.93 (d, 1H, *J* 7, py 3-H), 8.08 (dt, 1H, *J* 7, 1, py 4-H) and 9.11 (d, 1H, *J* 5.5 Hz, py 6-H); minor isomer δ 2.07 (s, 9H, C_6Me_3), 4.84 (dd, 1H, *J* 8, 7.5, OCH), 5.20 (m, 1H, OCH), 5.38 (s, 3H, $C_6H_3Me_3$), 5.39 (m, 1H, NCH), 7.44 (m, 3H, Ph), 7.58 (m, 2H, Ph), 7.87 (m, 1H, py 5-H), 7.99 (d, 1H, *J* 7, py 3-H), 8.12 (t, 1H, *J* 7, py 4-H) and 9.29 (d, 1H, *J* 5.5 Hz, py 6-H). MS (FAB$^+$): *m*/*z* 481, [M]$^+$.

[RuCl(Bz-pymox)(mes)][SbF$_6$] ***4***. Complex **4** was prepared from $[RuCl_2(mes)]_2$ (100 mg, 0.17 mmol), Bz-pymox (90 mg, 0.38 mmol) and $NaSbF_6$ (93 mg, 0.36 mmol) in 228 mg yield, 91%. mp 241 °C. Calc. for $C_{24}H_{26}ClF_6N_2ORuSb$: C, 39.45; H, 3.59; N, 3.83. Found: C, 40.37; H, 3.90; N, 3.58%. ^{1}H NMR: δ 2.22 (s, 9H, C_6Me_3), 2.63 (dd, 1H, *J* 14.5, 11, CH_2Ph), 3.40 (dd, 1H, *J* 14.5, 3.5, CH_2Ph), 4.55 (dd, 1H, *J* 9, 5.5, OCH), 4.84 (t, 1H, *J* 9, OCH), 5.10 (m, 1H, NCH), 5.28 (s, 3H, $C_6H_3Me_3$), 7.11–7.38 (m, 5H, Ph), 7.70 (m, 1H, py 5-H), 7.83 (d, 1H, *J* 8, py 3-H), 8.04 (dt, 1H, *J* 8, 1.5, py 4-H) and 9.02 (d, 1H, *J* 5.5 Hz, py 6-H). MS (FAB$^+$): *m*/*z* 495, [M]$^+$. [*a*] 256 (*c* = 0.125, CH_2Cl_2).

[RuCl(^{i}Pr-pymox)(mes)][SbF$_6$] ***5***. Complex **5** was prepared from $[RuCl_2(mes)]_2$ (100 mg, 0.17 mmol), ^{i}Pr-pymox (72 mg, 0.38 mmol) and $NaSbF_6$ (93 mg, 0.36 mmol) in 215 mg yield, 92%. mp 236–238 °C (decomp.) (Calc. for PF_6 salt. $C_{20}H_{26}ClF_6N_2ORuP$: C, 40.58; H, 4.43; N, 4.02. Found: C, 40.80; H, 4.18; N, 3.94%. ^{1}H NMR: δ 0.77 and 1.02 (2 × d, 2 × 3H, *J* 7 Hz, CH*Me*$_2$), 2.23 (m, 1H, C*H*Me$_2$), 2.25 (s, 9H, C_6Me_3), 4.82 (m, 2H, NCH + OCH), 5.00 (t, 1H, *J* 11, OCH), 5.34 (s, 3H, $C_6H_3Me_3$), 7.73 (m, 1H, py 5-H), 7.86 (d, 1H, *J* 7, py 3-H), 8.07 (dt, 1H, *J* 7.5, 1.5, py 4-H) and 9.01 (d, 1H, *J* 5 Hz, py 6-H). MS (FAB$^+$): *m*/*z*, 447 [M]$^+$; and 412, [M − Cl]$^+$. [*a*] 387 (*c* = 0.166, CH_2Cl_2).

[RuCl(^{t}Bu-pymox)(mes)][SbF$_6$] ***6***. Complex **6** was prepared from $[RuCl_2(mes)]_2$ (100 mg, 0.17 mmol), ^{t}Bu-pymox (77 mg, 0.38 mmol) and $NaSbF_6$ (93 mg, 0.36 mmol), in 217 mg yield, 91%). Calc. for $C_{21}H_{28}ClF_6N_2ORuSb$: C, 36.20; H, 4.05; N, 4.02. Found: C, 36.33; H, 3.71; N, 3.94%. ^{1}H NMR: δ 0.99 (s, 9H, CMe$_3$), 2.19 (s, 9H, C_6Me_3), 4.47 (dd, 1H, *J* 10, 4, OCH), 4.85 (m, 2H, NCH + OCH), 5.14 (s, 3H, $C_6H_3Me_3$), 7.69 (m, 1H, py 5-H), 7.82 (d, 1H, *J* 8, py 3-H), 8.02 (td, 1H, *J* 8, 1, py 4-H) and 8.92 (d, 1H, *J* 5 Hz, py 6-H). MS (FAB$^+$): *m*/*z* 461, [M]$^+$.

*[RuCl(^{i}Pr-pymox)(*p*-MeC$_6$H$_4$Pr^i)][SbF$_6$]* ***7***. Complex **7** was prepared from $[RuCl_2(p\text{-cymene})]_2$ (65 mg, 0.106 mmol),

^{i}Pr-pymox (41 mg, 0.22 mmol) and $NaSbF_6$ (51 mg, 0.22 mmol) in 123 mg yield, 83%. Calc. for $C_{21}H_{28}ClF_6N_2ORuSb$: C, 36.20; H, 4.05; N, 4.02. Found: C, 36.59; H, 4.19; N, 3.91%. ^{1}H NMR: S_{Ru} isomer δ 0.84 and 1.12 (2 × d, 2 × 3H, *J* 7, CH*Me*$_2$), 1.07 and 1.16 (2 × d, 2 × 3H, *J* 6, Ar-CH*Me*$_2$), 2.20 (s, 3H, Ar *Me*), 2.29 (m, 1H, C*H*Me$_2$), 2.77 (m, 1H, C*H*Me$_2$), 4.80 (m, 1H, OCH), 4.94 (m, 1H, NCH), 5.10 (t, 1H, *J* 9, OCH), 5.80 (m, 3H, Ar H), 5.91 (d, 1H, *J* 6, Ar H), 7.85 (m, 2H, py H) 8.09 (m, 1H, py H) and 9.30 (d, 1H, *J* 5.5 Hz, py 6-H); R_{Ru} isomer δ 0.84 and 1.12 (2 × d, 2 × 3H, *J* 7, CH*Me*$_2$), 1.07 and 1.16 (2 × d, 2 × 3H, *J* 6, Ar CH*Me*$_2$), 2.23 (s, 3H, Ar *Me*), 2.29 (m, 1H, C*H*Me$_2$), 2.77 (m, 1H, C*H*Me$_2$), 4.42 (m, 1H, NCH), 4.80 (m, 2H, NCH + OCH), 4.94 (m, 1H, NCH), 5.10 (t, 1H, *J* 9, OCH), 5.69 (m, 2H, Ar H), 5.80 (m, 1H, Ar H), 6.08 (d, 1H, *J* 6, Ar H), 7.85 (m, 2H, py H), 8.09 (m, 1H, py H) and 9.50 (d, 1H, *J* 5.5 Hz, py 6-H). MS (FAB$^+$): *m*/*z* 462, [M + H]$^+$.

[RuCl(^{t}Bu-pymox)(p-MeC$_6$H$_4$Pr^{i})][SbF$_6$] ***8.*** Complex **8** was prepared from [RuCl$_2$(*p*-MeC$_6$H$_4$Pr^{i})]$_2$ (70 mg, 0.114 mmol), ^{t}Bu-pymox (50 mg, 0.23 mmol) and $NaSbF_6$ (60 mg, 0.232 mmol) in 136 mg yield, 84%. Calc. for $C_{22}H_{30}ClF_6N_2ORuSb$: C, 37.18; H, 4.25; N, 3.94. Found: C, 37.41; H, 4.35; N, 3.83%. ^{1}H NMR: δ 1.06 (m, 6H, CH*Me*$_2$), 1.08 (s, 9H, CMe$_3$), 2.27 (s, 3H, Ar *Me*), 2.65 (sept, 1H, C*H*Me$_2$), 4.70 (dd, 1H, *J* 8, 4, NCH), 4.95 (m, 2H, OCH$_2$), 5.56, 5.67, 5.77 and 5.97 (4 × d, 4 × 1H, *J* 6, Ar H), 7.84 (m, 2H, py H), 8.11 (t, 1H, *J* 8, py 4-H) and 9.27 (d, 1H, *J* 5 Hz, py 6-H). MS (FAB$^+$): *m*/*z* 476, [M + H]$^+$.

[RuCl(^{i}Pr-pymox)(C$_6$H$_6$)][SbF$_6$] ***9.*** Complex **9** was prepared from [RuCl$_2$(C$_6$H$_6$)]$_2$ (50 mg, 0.10 mmol), ^{i}Pr-pymox (40 mg, 0.21 mmol) and $NaSbF_6$ (53 mg, 0.205 mmol) in 106 mg yield, 83%. Calc. for $C_{17}H_{20}ClF_6N_2ORuSb$: C, 31.87; H, 3.15; N, 4.37. Found: C, 31.52; H, 3.06; N, 3.93%. ^{1}H NMR: S_{Ru} isomer δ 0.87 and 1.06 (2 × d, 2 × 3H, *J* 7, CH*Me*$_2$), 2.50 (m, 1H, C*H*Me$_2$), 5.06 (m, 2H, 2 × OCH), 5.19 (m, 1H, NCH), 6.21 (s, 6H, C$_6$H$_6$), 7.92 (m, 1H, py H), 8.05 (m,1H, py H), 8.33 (m, 1H, py H) and 9.63 (d, 1H, *J* 3.5 Hz, py 6-H); R_{Ru} isomer δ 1.10 and 1.14 (2 × d, 2 × 3H, *J* 7, CH*Me*$_2$) 2.88 (m, 1H, C*H*Me$_2$), 4.57 (ddd, 1H, *J* 10, 7, 3.5, NCH), 4.93 (t, 1H, *J* 10, OCH), 5.06 (m, 1H, OCH), 6.21 (s, 6H, C$_6$H$_6$), 7.92 (m, 1H, py H), 8.05 (m, 1H, py H), 8.33 (m, 1H, py H) and 9.73 (d, 1H, *J* 3.5 Hz, py 6-H). MS (FAB$^+$): *m*/*z* 406, [M + H]$^+$.

[RuCl(^{t}Bu-pymox)(C$_6$H$_6$)][SbF$_6$] ***10.*** Complex **10** was prepared from [RuCl$_2$(C$_6$H$_6$)]$_2$ (60 mg, 0.12 mmol), ^{t}Bu-pymox (55 mg, 0.246 mmol) and $NaSbF_6$ (63 mg, 0.243 mmol) in 130 mg yield, 83%. Calc. for $C_{18}H_{22}ClF_6N_2ORuSb$: C, 33.03; H, 3.39; N, 4.28. Found: C, 33.35; H, 3.52; N, 4.15%. ^{1}H NMR: δ 1.09 (s, 9H, CMe$_3$), 4.61 (dd, 1H, *J* 10, 7, NCH), 4.90 (dd, 1H, *J* 10, 7, OCH), 5.02 (t, 1H, *J* 10, OCH), 5.93 (s, 6H, C$_6$H$_6$), 7.77 (m, 1H, py 5-H), 7.88 (d, 1H, *J* 7, py 3-H), 8.15 (t, 1H, *J* 7, py 4-H) and 9.19 (d, 1H, *J* 5 Hz, py 6-H). MS (FAB$^+$): *m*/*z* 420 [M + H]$^+$.

[RuCl(^{i}Pr-pymox)(C$_6$Me$_6$)][SbF$_6$] ***11.*** Complex **11** was prepared from [RuCl$_2$(C$_6$Me$_6$)]$_2$ (90 mg, 0.135 mmol), ^{i}Pr-pymox (54 mg, 0.28 mmol) and $NaSbF_6$ (73 mg, 0.28 mmol) in 185 mg yield, 95%. Calc. for $C_{23}H_{32}ClF_6N_2ORuSb$: C, 38.12; H, 4.45; N, 3.87. Found: C, 37.42; H, 4.26; N, 3.23%. ^{1}H NMR: δ 0.70 and 1.03 (2 × d, 2 × 3H, *J* 6.5, CH*Me*$_2$), 2.06 (m, 1H, C*H*Me$_2$), 2.18 (s, 6H, C$_6$Me$_6$), 4.71 (m, 1H, NCH), 4.81 (d, 1H, *J* 9, 4.5, OCH), 5.00 (t, 1H, *J* 9, OCH), 7.77 (dd, 1H, *J* 7.5, 5.5, py 5-H), 7.88 (d, 1H, *J* 7.5, py 3-H), 8.06 (t, 1H, *J* 7.5, py 4-H) and 8.84 (d, 1H, *J* 5.5 Hz, py 6-H). MS (FAB$^+$): *m*/*z* 489, [M]$^+$.

[RuCl(indanyl-pymox)(mes)][SbF$_6$] ***12.*** Complex **12** was prepared from [RuCl$_2$(mes)]$_2$ (80 mg, 0.137 mmol), indanyl-pymox (66 mg, 0.28 mmol) and $NaSbF_6$ (73 mg, 0.28 mmol) in 175 mg yield, 88%. Calc. for $C_{24}H_{24}ClF_6N_2ORuSb$: C, 39.56; H, 3.32; N, 3.84. Found: C, 39.68; H, 3.34; N, 3.80%. ^{1}H NMR: δ 2.23 (s, 9H, C$_6$Me$_3$), 3.54 (m, 2H, CH_2Ar), 5.38 (s, 3H, C$_6H_3$Me$_3$), 6.13 (ddd, 1H, *J* 8, 6, 2, OCH), 6.20 (d, 1H, *J* 8, NCH), 7.27 (m, 3H, Ar H), 7.53 (d, 1H, *J* 7, Ar H), 7.66 (m, 1H, py 5-H), 7.80 (d, 1H, *J* 9, py 3-H), 8.00 (td, 1H, *J* 8, 1, py 4-H) and 8.96 (d, 1H, *J* 6 Hz, py 6-H). MS (FAB$^+$): *m*/*z* 493, [M]$^+$.

[Ru(OH$_2$)(pymox)(arene)][SbF$_6$]$_2$ 13–24. A solution of $AgSbF_6$ (1 equivalent) in acetone (0.5 cm^3) was added to a solution of [RuCl(pymox)(arene)][SbF$_6$] **1**–**12** (one equivalent) in CH_2Cl_2 (4 cm^3), giving a yellow-orange solution and an immediate precipitate of AgCl. The solution was stirred for 30 min at room temperature (protected from light), then filtered through Celite in air to remove AgCl; thus the water ligand may arise from the work-up. Evaporation, followed by washing with CH_2Cl_2, afforded the aqua complexes as orange oils. In some cases the products could be recrystallised from acetone–diethyl ether, affording a crop of fine needles. As an example, the preparation of **17** is shown below. The spectroscopic data of **13**–**24** are very similar to those of the respective precursor chlorides **1**–**12** therefore the exact quantities of reagents used, yields obtained (76–96%), ^{1}H NMR and mass spectrometry data and in certain cases elemental analyses are given in the ESI supplementary material.

[Ru(OH$_2$)(^{i}Pr-pymox)(mes)][SbF$_6$]$_2$ 17. Complex **17** was prepared from **5** (100 mg, 0.147 mmol), and $AgSbF_6$ (52 mg, 0.15 mmol) in 121 mg yield, 92%. Calc. for $C_{20}H_{28}F_{12}N_2O_2RuSb_2$: C, 26.66; H, 3.13; N, 3.11. Found: C, 26.37; H, 2.87; N, 3.04%. ^{1}H NMR (CD_2Cl_2–d$_6$-acetone, 10 : 1): δ 0.57 and 1.01 (2 × d, 3H, *J* 7, CH*Me*$_2$), 2.20 (m, 1H, C*H*Me$_2$), 2.22 (s, 9H, C$_6$Me$_3$), 4.78 (dd, 1H, *J* 8.5, 5, OCH), 4.92 (m, 1H, NCH), 5.03 (t, 1H, *J* 9, OCH), 5.40 (br s, 2H, H_2O), 5.55 (s, 3H, C$_6H_3$Me$_3$), 7.87 (m, 2H, py H), 8.15 (t, 1H, *J* 8, py 4-H) and 9.40 (d, 1H, *J* 5 Hz, py 6-H). MS (FAB$^+$): *m*/*z*, 647 [M − OH$_2$ + SbF$_6$]$^+$; and 429, [M − H]$^+$.

[Ru(CH$_2$CMeCHO)(^{i}Pr-pymox)(mes)][SbF$_6$]$_2$ 25. Complex **25** was prepared from **5** (15 mg, 0.022 mmol), $AgSbF_6$ (0.029 mmol) and $CH_2CMeCHO$ (2.2 μl, 0.026 mmol) in CD_2Cl_2 (1 ml) in the presence of activated molecular sieves. The reaction vessel was covered in aluminium foil to protect it from light, and after stirring for 1 h the solution was filtered into an NMR tube and the ^{1}H NMR spectrum was obtained. ^{1}H NMR: δ 0.70 and 1.15 (2 × d, 2 × 3H, *J* 7, CH*Me*$_2$), 1.74 (s, 3H, *Me*C=CH$_2$), 2.30 (s + m, 10H, C$_6$Me$_3$ + C*H*Me$_2$), 4.89 (m, 1H, OCH), 5.12 (m, 1H, OCH), 5.38 (m, 1H, NCH), 5.65 (s, 3H, C$_6H_3$Me$_3$), 6.59 (s, 1H, MeC=CH_2), 6.70 (s, 1H, MeC=CH_2), 8.00 (m, 1H, py 5-H), 8.10 (td, 1H, *J* 5.5, 1.5, py 3-H), 8.29 (m, 1H, py 4-H), 9.10 (s, 1H, CHO) and 9.62 (d, 1H, *J* 5 Hz, py 6-H).

Crystal structure determinations

Details of the structure determinations of crystal of complexes **1**, **3** and **12** are given in Table 4; those for **5** have been described previously.[19] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional restraints. Complex **1** has two independent molecules in the unit cell; the only differences are a slight rotation of the mesitylene ring about the Ru–ring axis and a small deviation from planarity in the oxazoline ring of one of the molecules.

CCDC reference number 186/2231.

See http://www.rsc.org/suppdata/dt/b0/b006530g/ for crystallographic files in .cif format.

Catalysis

Schlenk reactions (under N$_2$). Methacrolein (1 mmol) and 2,6-di-*tert*-butylpyridine (1 equivalent per mol catalyst) were added to a suspension of the appropriate dication **13**–**24** (0.1, 0.2, or 0.5 mmol) in CH_2Cl_2 (2 cm^3). The resulting yellow solution was cooled to the appropriate temperature before addition of cyclopentadiene (2 mmol). At the end of the reactions the mixture was passed through a plug of silica, the solvent removed and the product obtained as a colourless oil. The

Table 4 Crystallographic data for complexes **1**, **3** and **12**

	1	**3**	**12**
Empirical formula	$C_{19}H_{24}ClF_6N_2ORuSb$	$C_{50}H_{50}BClN_2O_2Ru$	$C_{24}H_{24}ClF_6N_2ORuSb$
M	668.67	858.25	728.72
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$
a/Å	14.912(2)	12.446(2)	11.524(3)
b/Å	14.169(4)	12.770(5)	11.672(2)
c/Å	21.961(4)	26.884(3)	19.208(7)
β/°	97.32(1)		
U/Å^3	4602(1)	4273(2)	2583(1)
Z	8	4	4
T/K	200(2)	190(2)	190(2)
μ/mm^{-1}	2.008	0.471	1.797
Reflections collected	11201	5652	6784
Unique reflections (R_{int})	9987 (0.0442)	5422 (0.0173)	5463 (0.0381)
$R1$ indices [$I > 2\sigma(I)$]	0.0553	0.0444	0.0428
$wR2$ (all data)	0.1446	0.1196	0.1094
Flack parameter		−0.02(5)	−0.06(4)

Crystallographic data for complex **5** has been published in ref. 19.

exo:*endo* ratio was determined by ^{1}H NMR spectroscopy and the enantiomeric excess by ^{1}H NMR or GC after conversion into the acetal with (2*R*, 4*R*)-pentanediol.[28] The catalyst could also be prepared *in situ* from the chloride complexes **1**–**12** and one equivalent of $AgSbF_6$ in CH_2Cl_2, filtration through Celite into a Schlenk tube to remove AgCl and then addition of the reagents as described above.

NMR tube experiments (in air). The dienophile (0.25 mmol) was added to a suspension of catalyst (5 μmol) in CD_2Cl_2 (0.5 cm^3) which led to rapid dissolution of catalyst to give a yellow solution. The solution was transferred to an NMR tube and 2,6-di-*tert*-butylpyridine (1 equivalent per mol catalyst) and diene (0.5 mmol) were added. The ^{1}H NMR spectrum was run immediately and then repeated after suitable time intervals. The *exo*:*endo* ratio and enantiomeric excess were determined as described above.

Acknowledgements

We thank the EPSRC for a studentship (A. J. D.), the University of Leicester for a studentship (S. A. G.), the EPSRC chiroptical spectroscopy service for preliminary circular dichroism measurements, Johnson Matthey for the loan of $RuCl_3$ and NSC Technologies for gifts of phenylglycinol [$H_2NCH(Ph)CH_2OH$] and *tert*-butylglycine [$H_2NCH(^tBu)CO_2H$].

References

1 G. Consiglio and F. Morandini, *Chem. Rev.*, 1987, **87**, 761; H. Brunner, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 1194.
2 V. I. Sokolov, *Chirality and optical activity in organometallic compounds*, Gordon and Breach Science Publishers, New York, 1990.
3 H. Brunner, *Adv. Organomet. Chem.*, 1980, **18**, 151.
4 S. G. Davies, *Pure Appl. Chem.*, 1988, **60**, 13.
5 J. W. Faller, M. R. Mazzieri, J. T. Nguyen, J. Parr and M. Tokunaga, *Pure Appl. Chem.*, 1994, **66**, 1463.
6 E. P. Kundig, A. Quattropani, M. Inage, A. Ripa, C. Dupré, A. F. J. Cunningham and B. Bourdin, *Pure Appl. Chem.*, 1996, **68**, 97.
7 R. Noyori and S. Hashiguchi, *Acc. Chem. Res.*, 1997, **30**, 97.
8 W. S. Sheldrick and S. Heeb, *J. Organomet. Chem.*, 1989, **377**, 357; D. F. Dersnah and M. C. Baird, *J. Organomet. Chem.*, 1977, **127**, C55; W. S. Sheldrick and S. Heeb, *Inorg. Chim. Acta*, 1990, **168**, 93; G. Capper, D. L. Davies, J. Fawcett and D. R. Russell, *Acta Crystallogr.*, *Sect. C*, 1995, **51**, 578; L. C. Carter, D. L. Davies, K. T. Duffy, J. Fawcett and D. R. Russell, *Acta Crystallogr.*, *Sect. C*, 1994, **50**, 1559; D. Carmona, A. Medoza, F. J. Lahoz, L. A. Oro, M. P. Lamata and E. San Jose, *J. Organomet. Chem.*, 1990, **396**, C17; D. Carmona, C. Vega, F. J. Lahoz, R. Atencio, L. A. Oro, P. M. Lamata, F. Viguri and E. San Jose, *Organometallics*, 2000, **19**, 2273; R. Kramer, K. Polborn, H. Wanjek, I. Zahn and W. Beck, *Chem. Ber.*, 1990, **123**, 767.
9 S. K. Mandal and A. R. Chakravarty, *J. Organomet. Chem.*, 1991, **417**, C 59; S. K. Mandal and A. R. Chakravarty, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 1627; S. K. Mandal and A. R. Chakravarty, *Inorg. Chem.*, 1993, **32**, 3851.
10 (*a*) H. Brunner, R. Oeschey and B. Nuber, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 1499; (*b*) H. Brunner, R. Oeschey and B. Nuber, *J. Organomet. Chem.*, 1996, **518**, 47; (*c*) H. Brunner, R. Oeschey and B. Nuber, *Inorg. Chem.*, 1995, **34**, 3349; (*d*) H. Brunner, T. Neuhierl and B. Nuber, *Eur. J. Inorg. Chem.*, 1998, 1877; (*e*) H. Brunner and M. Prommesberger, *Tetrahedron: Asymmetry*, 1998, **9**, 3231; (*f*) H. Brunner, B. Nuber and M. Prommesberger, *Tetrahedron: Asymmetry*, 1998, **9**, 3223.
11 D. L. Davies, J. Fawcett, R. Krafczyk and D. R. Russell, *J. Organomet. Chem.*, 1997, **545**–**546**, 581.
12 D. Carmona, C. Vega, F. J. Lahoz, S. Elipe, L. A. Oro, P. M. Lamata, F. Viguri, R. Garcia-Correas, C. Cativiela and M. P. Lopez-Ram deViu, *Organometallics.*, 1999, **18**, 3364.
13 H. Brunner, R. Oeschey and B. Nuber, *Organometallics*, 1996, **15**, 3616.
14 S. Attar, J. H. Nelson, J. Fischer, A. Decian, J. P. Sutter and M. Pfeffer, *Organometallics*, 1995, **14**, 4559; S. Attar, V. J. Catalano and J. H. Nelson, *Organometallics*, 1996, **15**, 2932; N. Gul and J. H. Nelson, *Organometallics*, 1999, **18**, 709; N. Gul and J. H. Nelson, *Polyhedron*, 1999, **18**, 1835; H. D. Hansen, K. Maitra and J. H. Nelson, *Inorg. Chem.*, 1999, **38**, 2150.
15 D. Enders, H. Gielen, G. Raabe, J. Runsink and J. H. Teles, *Chem. Ber./Recueil*, 1997, **130**, 1253.
16 M. Otto, J. Parr and A. M. Z. Slawin, *Organometallics*, 1998, **17**, 4527.
17 (*a*) J. Faller, B. P. Patel, M. A. Albrizzio and M. Curtis, *Organometallics*, 1999, **18**, 3096; (*b*) J. Faller and J. Parr, *Organometallics*, 2000, **19**, 1829.
18 C. G. Arena, S. Calamia, F. Faraone, C. Graiff and A. Tiripicchio, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 3149.
19 D. L. Davies, J. Fawcett, S. A. Garratt and D. R. Russell, *Chem. Commun.*, 1997, 1351.
20 H. Asano, K. Katayama and H. Kurosawa, *Inorg. Chem.*, 1996, **35**, 5760.
21 D. Carmona, C. Cativiela, S. Elipe, F. J. Lahoz, M. P. Lamata, M. P. Lopez-Ram de Viu, L. A. Oro, C. Vega and F. Viguri, *Chem. Commun.*, 1997, 2351.
22 H. Brunner, R. Oeschey and B. Nuber, *Inorg. Chem.*, 1995, **34**, 3349.
23 H. Brunner and T. Zwack, *Organometallics*, 2000, **19**, 2423.
24 A. J. Davenport, D. L. Davies, J. Fawcett, S. A. Garratt and D. R. Russell, *Chem. Commun.*, 1999, 2331.
25 P. E. Hansen, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1988, **20**, 207.
26 T. K. Hollis, W. Odenkirk, N. P. Robinson, J. Whelan and B. Bosnich, *Tetrahedron*, 1993, **49**, 5415.
27 E. P. Kundig, C. M. Saudan and G. Bernardinelli, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 1220.
28 D. A. Evans, J. A. Murry, P. v. Matt, R. D. Norcross and S. J. Miller, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 798.

29 For conformational studies on Lewis acid methacrolein complexes see, K. Ishihara, Q. Gao and H. Yamamoto, *J. Am. Chem. Soc.*, 1993, **115**, 10412 and references therein.
30 K. Furuta, S. Shimizu, Y. Miwa and H. Yamamoto, *J. Org. Chem.*, 1989, **54**, 1481.
31 K. Ishihara, Q. Gao and H. Yamamoto, *J. Org. Chem.*, 1993, **58**, 6917.
32 E. P. Kundig, B. Bourdin and G. Bernardinelli, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 1856.
33 H. Brunner and U. Obermann, *Chem. Ber.*, 1989, **122**, 499.
34 C. Bolm, K. Weickharott, M. Zender and T. Ranff, *Chem. Ber.*, 1991, **124**, 1173.
35 M. J. McKennon, A. I. Meyers, K. Drauz and M. Scharm, *J. Org. Chem.*, 1993, **58**, 3568.
36 J. W. Hull, Jr. and W. L. Gladfelter, *Organometallics*, 1984, **3**, 605.
37 M. A. Bennett, T. Huang, T. W. Matheson and A. K. Smith, *Inorg. Synth.*, 1982, **21**, 75.