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Salen ligands derived from *trans*-1,2-dimethyl-1,2-cyclohexanediamine: preparation and application in oxo-chromium salen mediated asymmetric epoxidation of alkenes

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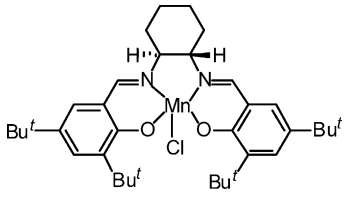
Abstract

Syntheses of two novel chiral non-racemic salen ligands and four of their chromium(III) complexes are described. The ligands were derived from resolved *trans*-1,2-dimethyl-1,2-cyclohexanediamine. The complexes were evaluated as asymmetric epoxidation catalysts in the stoichiometric asymmetric epoxidation of *E*- and *Z*-β-methylstyrene and proved disappointing. Elecrotrospray MS of the complexes and single crystal X-ray structure determination of one of the salen ligands was performed. This gave insight as to why the catalysts did not perform as expected on the basis of the existance of multiple oxidants in the system. Some additional details of the synthesis of the diamine are also reported.

Keywords: Chromium; Salen; Epoxidation; Asymmetric; Trans-1,2-dimethyl-1,2-cyclohexanediamine

1. Introduction

Over the last two decades there have a number of important advances in the development of general methods for catalytic asymmetric alkene epoxidation. The best of these include the systems of Sharpless [1] and Jacobsen/Katsuki [2,3]. Notably, the relatively accessible Jacobsen's catalyst **1** and analogues of it allow the asymmetric epoxidation of unfunctionalised alkenes, with bleach as stoichiometric oxidant, to proceed in high enantioselectivity (>90% ee for *Z*- and tri-substituted alkenes) [4–6]. However, a major limitation of Jacobsen's catalyst is that low selectivity is observed in the epoxidation of *E*-1,2-disubstituted alkenes (<30% ee) [3,4,7].



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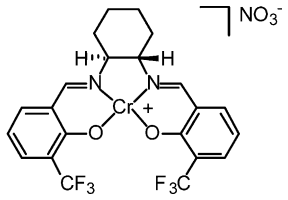

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In recent years our group has been working on the development of epoxidation catalysts based on a chromium salen template [6,8–16]. These show a contrasting selectivity pattern to their manganese analogues in that they allow the asymmetric

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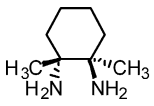
epoxidation, with iodosylbenzene as stoichiometric oxidant, of *E*-1,2-disubstituted with high enantioselectivity (>90% ee with complex 2) [8,12]. A major advantage of this system is that reactions can be studied stoichiometrically as well as the catalytic level thus allowing study of stereoselectivity separated from catalytic cycle issues. Thus, for example, $(salenCr(V)=O)^+$ (oxo-2) can be isolated and used in a 1:1 reaction with alkene, thus revealing the true stereoselectivity of the epoxidation step. We utilise this aspect in the present work to gain insight into the mode of action of these catalytic systems. Very recently in the manganese series, both theoretical and experimental evidence has been reported [17] which suggests that there are other oxidising species in the reaction in addition to (salen)*M*(*V*) = *O* and this is a subject of ongoing current interest. In the present work we find that our results may be interpreted on the basis of additional oxidants.

As part of the ongoing investigation [11] by our group into the effect of the diamine backbone on enantioselectivity in chromium-salen catalysed asymmetric epoxidation we decided to prepare complexes derived from enantiomers of *trans*-1,2-dimethyl-1,2-cyclohexanediamine **3**. Although only mediocre results of oxidations using salen complexes derived from **3** had been reported [4,18], we believed that the chromium analogues were more promising. This was because we [6,9,13,14] and others [19–22] had suggested that the stereoselection obtained using manganese and chromium salen complexes is related to non-planarity of the N_2O_2 ligand core of the complex. This non-planarity has been observed in a number of X-ray crystal structures [20] and arises as a result of the sp^3 centres on the ethylene bridge of the ligand. Thus, the N–C–C–N dihedral angle is a measure of the resultant twist or step in the complex. We had previously suggested that chromium salen complexes facilitate selective epoxidation of *E*-alkenes by their more stepped nature [6,14] and so we believed that the presence of methyl groups in the 1- and 2-positions on the cyclohexane ring would cause a conformational change (more twist) in the catalyst resulting in a positive effect on the selectivity of the system.



R,R-**3**

2. Results and discussion

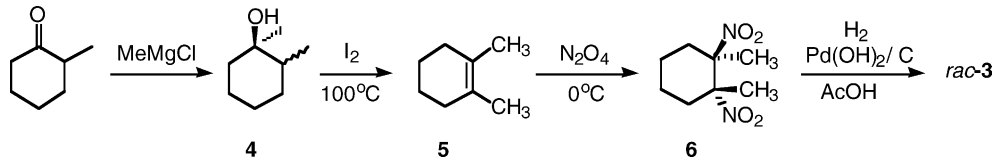
Only one synthesis of the enantiopure diamine has been reported: that of Zhang and Jacobsen [23]. Therefore, we undertook a modified version of their synthesis (Scheme 1). Due to the ready availability of 1,2-dimethylcyclohexanol 4 we decided to prepare the pivotal 1,2-dimethylcyclohexene 5 from this starting material. This was in contrast to the route taken by Jacobsen and Zhang [23], who prepared 5 from *ortho*-xylene via a Birch reduction/Wilkinson hydrogenation sequence [24].

2.1. Synthesis of salen ligands

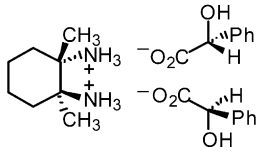
The procedure of Signaigo and Cramer [25] was followed for the preparation of alkene 5. Alcohol 4 was prepared by the Grignard synthesis as a mixture (3:7) of *cis* and *trans* isomers in an overall yield of 71% after fractional distillation. This mixture was then dehydrated [25] by heating to 100 °C in the presence of iodine with slow distillation of the reaction mixture. Work-up and fractional distillation gave an alkene mixture that was found to consist of the desired 1,2-dimethylcyclohexene 5 (72%), along with 1,6-dimethylcyclohexene (21%) and 2-methylmethylenecyclohexane (7%) as indicated by ^{1}H NMR analysis [26]. It is interesting to note that the proportion of 1,2-dimethylcyclohexene in the alkene mixture by the Zhang/Jacobsen route [23] (77%) is quite similar to that obtained using the Signaigo/Cramer route [25] (72%).

Following Boyer and Evans [27], slow addition of the crude alkene mixture, containing mainly alkene 5, to an ethereal solution of dinitrogen tetroxide at 0 °C led to a mixture containing substantial amounts of *trans*-1,2-dimethyl-1,2-dinitrocyclohexane 6 and several impurities, one of which was quite abundant. The presence of compound 6 was confirmed by agreement of its NMR data with the literature [23,27] and by X-ray crystallography of its derivatives (vide infra). The significant impurity had a diagnostic ^{1}H NMR signal at δ 1.79 ppm (singlet) and was always found in the crude reaction mixture in amounts varying from reaction to reaction up to 49%. Zhang and Jacobsen had reported a very high (>30:1) *trans* selectivity and did not allude to impurities other than starting *o*-xylene and 1,6-dimethylcyclohexene [23]. In our case, the other alkene impurities can be discounted as being the source of the major impurity as their dinitro derivatives would not account for the ^{1}H NMR signals of the impurity. We also discounted the possibility of it being the other *trans*-conformer and assume that it is the *cis*-isomer.

Following Zhang and Jacobsen [23], hydrogenation of 6 was carried out in glacial acetic acid with $Pd(OH)_2$ on carbon under 3 atmospheres of H_2. Our best yield for this step was 61%. The crude product was not purified further but instead was reacted with the resolving agent, (*S*)-(+)-mandelic acid (2 equiv.), to afford crystals of bis-(*S*)-mandelate which, after recrystallisation four times from ethanol, gave pure (*R*,*R*)-diamine bis-(*S*)-mandelate (ent-7) as judged by the constancy of specific rotation, $[\alpha]_D = +73.3^\circ$, and comparability to the literature value [23] of +72.6°. (*R*,*R*)-(−)-3 was then liberated by treatment with 1 M NaOH solution and used within one day. The mother liquor from the initial crystallisation was evaporated and treated with 1 M NaOH to release scalemic diamine from which the bis-(*R*)-mandelate was formed by reaction with (*R*)-(−)-mandelic acid giving an equal but opposite specific rotation. In this way the majority of the diamine was recovered. The absolute stereochemistry of the diamines was subsequently re-confirmed by X-ray crystallography studies (vide infra) on the bis-(*R*)-mandelate salt 7.



Scheme 1.



S,S,R,R-**7**

The salen ligands (*R*,*R*)-8 and (*S*,*S*)-9 were then prepared in good yield (83 and 80%, respectively) by simple condensation of the relevant diamine and salicylaldehyde. Both were fully characterised and the structure of 8 was confirmed by X-ray crystallography (vide infra).

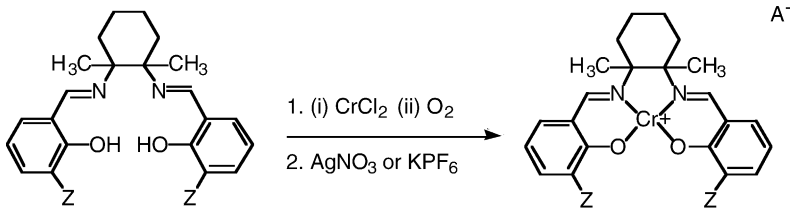
2.2. Preparation of chromium salen complexes

The (salen)Cr(III) complexes, (*R*,*R*)-10 and (*S*,*S*)-11 of these ligands were then prepared by reaction with anhydrous chromium(II) chloride [28], followed by air oxidation. Both complexes were afforded in moderate yields of 50% and 46% for (*R*,*R*)-10 and (*S*,*S*)-11 respectively and were characterised by IR spectroscopy with characteristic C=N stretches observed at 1625 cm^{-1} for (*R*,*R*)-10 and 1619 cm^{-1} for (*S*,*S*)-11. (*R*,*R*)-10 was also characterised by electrospray mass spectroscopy (vide infra). It should be noted that neither complex gave satisfactory microanalysis data. Initially, we were not unduly worried by this because it is very common in the preparation of chromium salen complexes [29,30]. It is often caused by the presence of an impurity arising from the $CrCl_2$ insertion process [31], which we have previously shown [12,32] is inactive in the oxidation process. Another reason for the discrepancy could be the number of solvent molecules that coordinate to the transition metal centre. In all our calculations we assumed that one molecule of water coordinated to the chromium(III) centre, Scheme 2.

(*R*,*R*)-10 was then allowed to react with silver nitrate yielding a precipitate of silver chloride and leading to the isolation of (*R*,*R*)-12 as a brown solid in a yield of 61%. In the IR spectrum, (*R*,*R*)-12 had C=N and N–O stretches at 1625 cm^{-1} and 1385 cm^{-1}, respectively. Similarly, (*S*,*S*)-11 was subjected to reaction with potassium hexafluorophosphate and (*S*,*S*)-13 was isolated as a brown precipitate in 43% yield and its IR spectrum showed C=N and P–F stretches at 1618 and 843 cm^{-1}, respectively.

2.3. Asymmetric epoxidation mediated by complexes (*R*,*R*)-12 and (*S*,*S*)-13

We evaluated the epoxidation of *E*- and *Z*-β-methylstyrene using stoichiometric amounts of complexes (*R*,*R*)-12 and (*S*,*S*)-13. Iodosylbenzene was used to generate oxo-12 and oxo-13 and the reactions were carried out both in the presence and absence of our standard donor ligand additive, triphenylphosphine oxide [8,12,15]. In all cases the yields did not exceed 20%, which is not unusual for these stoichiometric reactions [10]. The enantioselectivities obtained are presented in Table 1 and it can be seen that, preparatively, they are disappointing. The most interesting observation is that, in the epoxidation of *E*-β-methylstyrene, the effect of methyl substitution on the cyclohexyl ring is to dramatically decrease the level of asymmetric induction from that achieved with our previously reported [8,10] cyclohexyldiamine derived chromium salen catalysts (72–92% ee). Also, contrary to the effect previously observed with the cyclohexyl diamine analogues [8,12,15], the use of the additive (Ph_3PO) has a slightly negative or negligible effect on enantioselectivity. It is also notable that the effect of changing salen substitution (from H to CF_3) at the 3,3′-positions on the salen ring is rather muted in comparison to the leap in enantioselectivity (57–89% ee) seen for the cyclohexyl diamine analogues [10]. Clearly the effect of diamine substitution is highly significant and

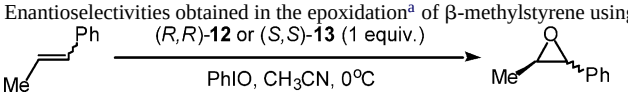


8: Z = CF_3
9: Z = H

10: Z = CF_3; A = Cl
11: Z = H; A = Cl
12: Z = CF_3; A = NO_3
13: Z = H; A = PF_6

Scheme 2.

Table 1
Enantioselectivities obtained in the epoxidation[a] of β-methylstyrene using chromium salen complexes (*R*,*R*)-12 and (*S*,*S*)-13



Substrate	Complex	Additive	Product e.e. (%)[b]	Product configuration[c]
E-β-methylstyrene	(*S*,*S*)-13	None	30	(2*S*,3*S*)
E-β-methylstyrene	(*S*,*S*)-13	Ph_3PO	33	(2*S*,3*S*)
E-β-methylstyrene	(*R*,*R*)-12	None	41	(2*R*,3*R*)
E-β-methylstyrene	(*R*,*R*)-12	Ph_3PO	35	(2*R*,3*R*)
Z-β-methylstyrene	(*S*,*S*)-13	None	22	(2*S*,3*R*)
Z-β-methylstyrene	(*S*,*S*)-13	Ph_3PO	23	(2*S*,3*R*)
Z-β-methylstyrene	(*R*,*R*)-12	None	28	(2*S*,3*R*)
Z-β-methylstyrene	(*R*,*R*)-12	Ph_3PO	27	(2*S*,3*R*)

[a] Cr(III) complex treated with PhIO initially, filtered and then treated with alkene, full details in Section 4. Yields were in the range 10–20%.
[b] Determined on cyclodextrin-based chiral stationary phase GLC columns, full details in Section 4.
[c] (2*R*,3*S*) refers to 2-methyl-3-phenyloxirane (β-methylstyrene oxide).

overrides the effect of either substitution on the aromatic ring of the salen ligand [16] or additives [15].

Different effects are seen in the epoxidation of *Z*-β-methylstyrene, Table 2. The low levels of selectivity displayed are quite similar to those observed with cyclohexyl diamine analogues (25–29% ee) [8,33]. However, it is notable that the effect of changing salen substitution (from H to CF_3) at the 3,3′-positions on the salen ring is to change the sense of enantioselectivity. At this point all cyclohexyl diamine- derived chromium salen epoxidation catalysts show poor selectivity for *Z*-alkenes.

2.4. Discussion of epoxidation results, ES/MS and X-ray crystallography studies

Previously we have been able to explain the selectivities obtained in the epoxidation of *E*-alkenes in terms of their different trajectories of approach to the oxochromium species [16]. The N–C–C–N dihedral angle of the cyclohexyl diamine is chiefly responsible for the excellent levels of enantioselectivity (up to 93% ee) obtained, by allowing a favourable conformation of the complex [15]. The unexpected and strongly negative effect of methyl substitution on the cyclohexyl diamine ring therefore runs counter to our expectations. Such a strong effect could be explained by blocking of the major trajectory of approach of the *E*-alkene towards the oxochromium species. However, we have shown previously that the major approach is not in the vicinity of the cyclohexyl backbone [16]. Alternatively, we could argue that the methyl substitution may have an unfavourable effect on the conformation of the complex resulting in a less selective catalyst. Again however, it is difficult to see how variations of conformation could lead to an almost complete loss of selectivity. We therefore looked elsewhere for an explanation of the poor results.

A possible clue came from ES/MS studies on complexes 10 and 12. These showed the presence of substantial amounts of species, the masses of which would correspond to dimeric and higher oligomeric complexes. This led us to consider whether the structures of the complexes synthesised may not be as shown in diagrams 10–13. In particular we considered that, if all else were equal, the methyl groups on the ligand should have taken up diequatorial positions, rather than the diaxial positions implied in 10–13. In turn this would force the two salicylaldimine substituents diaxial and thereby unable to co-ordinate to the same metal. If this were true, it would lead to the possibility of dimeric or polymeric contaminants resulting from different metal atoms co-ordinating the salicylaldimine moieties as shown in Fig. 1 [34]. In turn these complexes could act as alternative oxidising species in the reaction, potentially lowering the selectivity obtained.

Ideally we would like to have performed X-ray crystallography on the complexes. However, it has always been a difficulty in our studies that chromium salen complexes are notoriously difficult to crystallise [8,29,30] and therefore there is an almost complete lack of crystal structure determinations

Table 2
Effect of reaction conditions on the yield of *trans*-1,2-dimethyl-1,2- dinitrocyclohexanediamine 6 from alkene 5 according to Scheme 1

Temperature (°C)	Air/O_2	Addition time (h)	Crude yield (%)[a]	Impurity (%)[b]	Isolated yield (%)[a]
0	Air	6	23	18	16
0	Air	3	7	39	–
0	O_2	6	38	49	–
−21 to −10	Air	3	6	40	3
−42	Air	6	21	35	9

[a] Based on the percentage of 1,2-dimethylcyclohexene in the alkene mixture used.
[b] Impurity (%) in crude reaction mixture determined by NMR integration of the methyl signals in 6 and the impurity, assuming equality of the number of hydrogens in each and neglecting small amounts of other products.

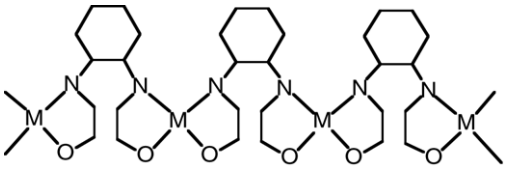


Fig. 1. Schematic representation of the possibility of oligomeric salen complexes, aromatic rings omitted for clarity.

on them [30,35]. This is caused by the presence of impurities noted previously. Unfortunately, despite our best efforts, complexes 10–13 proved not be exceptions to this. We therefore resorted to studies on their precursors.

We first studied the bis-(*R*)-mandelate salt 7. Zhang and Jacobsen [23] had noted that they had established the absolute stereochemistry of the diamine (*S*,*S*) from the relative stereochemistry of the mandelate ion in an X-ray crystal structure determination on this salt. However, they had reported no details of the study. We therefore re-examined this problem and confirmed the stereochemical assignment (Fig. 2). More interesting was the issue of the disposition of the ring substituents. Usually, when only information on electron densities and bond distances are available, it is hard to distinguish between methyl ($-CH_3$) and ammonium ion ($-NH_3$) groups. This may have been why Zhang and Jacobsen were unable to report the details of their X-ray studies. In the present work however, we found that we were able to locate all hydrogen atoms. This was because they were very well refined so that their positions were reliable. As only protons bonded to nitrogen are suitable for hydrogen bonding, this allowed a means of distinguishing the methyl group and ammonium groups. A careful examination of the surroundings of all methyl and ammonium groups showed that all X–H bonds in the ammonium groups point to suitable acceptors, but only one of the X–H bonds in each methyl group points towards an acceptor (they have to point somewhere). In addition, the putative hydrogen bond lengths observed for the ammonium groups are typical (183–213 pm) while the

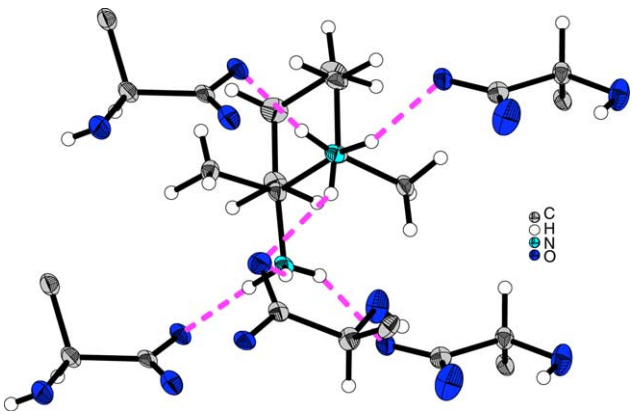


Fig. 2. ORTEP diagram of salt 7. The cation is shown with the anions connected to it by hydrogen bonding; the phenyl rings of the anions are omitted for clarity; thermal ellipsoids are drawn on the 50% probability level.

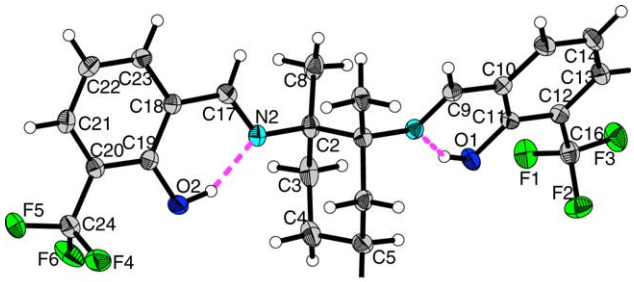


Fig. 3. ORTEP diagram of salen ligand (*R*,*R*)-8 thermal ellipsoids are drawn on the 50% probability level.

protons in the methyl groups are much further away from the mandelate oxygens (250–251 pm). Finally, exchanging C and N significantly degraded the refinement, especially of the hydrogen atoms. From the resulting crystal structure (Fig. 2) it is clear that the methyl groups take up axial positions while the ammonium mandelate groups take up equatorial positions.

However, when the diamine is released from its salt form, the resulting amino groups should take up axial positions due to their smaller space requirement vis-à-vis the methyl groups. The same might then be expected for the derived salicylaldimine groups. This was borne out when we examined the salen ligand 8 (Fig. 3). It can clearly be seen that the methyl groups are indeed in equatorial positions. This lends strong support to the hypothesis that the actual oxidising species may be oligomeric or polymeric complexes thereby leading to the loss of selectivity.

3. Conclusion

We have described the first synthesis of chromium salen complexes derived from *trans*-1,2-dimethyl-1,2-cyclohexanediamine. Two of these complexes were tested as epoxidation catalysts in the asymmetric epoxidation of *E*- and *Z*-β-methylstyrene. Both complexes afforded low levels of enantioselectivity in the epoxidation of *E*- and *Z*-β-methylstyrene. The *E*-alkene epoxidation results show that the diamine substitution is the dominant determinant of selectivity in this system. We have concluded that the poor selectivity results from the presence of multiple oxidants in the system. We also conclude that the diaxial disposition of the salicylaldimine groups in the salen ligands derived from *trans*-1,2-dimethyl-1,2-cyclohexanediamine means that this chiral controller group may never be useful for this type of catalysis.

4. Experimental

4.1. General experimental

Melting points were determined either on a Gallenkamp melting point block or a Reichert Thermovar and are uncor-

rected. Optical rotation values were obtained using a Perkin-Elmer 241 polarimeter. ^{1}H NMR spectra were recorded at 270 MHz on a JEOL JNM-GX270 FT spectrometer and at 300 MHz on a Varian INOVA 300 spectrometer. ^{13}C NMR spectra were recorded at 67 MHz (JEOL) or 75 MHz (Varian). Chemical shifts are reported as δ values in ppm relative to internal standard tetramethylsilane (TMS) for ^{1}H spectra. Chiral gas–liquid chromatography (GC) was performed on a Shimadzu GC-8A gas chromatograph coupled to a Shimadzu C-R3A integrator. All commercially available solvents were used as supplied, unless otherwise stated. Solvents were dried according to standard procedures [36]. Flash column chromatography was performed on Merck silica 9385, particle size 0.04–0.063 mm. Iodosylbenzene was prepared according to Saltzmann and Sharefkin [37]. *Z*-β-methylstyrene was obtained from Chemsampco Inc., 40 Enterprise Avenue, Trenton, NJ 08638, USA. All other chemicals were obtained from the Aldrich Chemical Company and used as received.

4.2. 1,2-dimethylcyclohexanol, 4

A procedure described by Signaigo and Cramer was employed [25]. Methylmagnesium chloride (187.5 mL of 3.0 M solution in THF, 0.56 mol) was added to a two-necked round-bottomed flask equipped with a dropping funnel. 2-Methylcyclohexanone (49.9 g, 0.45 mol) in diethyl ether (200 mL) was added slowly to the cooled, stirred Grignard reagent. Throughout the addition the temperature of the reaction mixture was kept below 5 °C by cooling on ice. After 5 h all of the ketone had been added. The reaction mixture was allowed to warm to room temperature and was then hydrolysed with saturated ammonium chloride solution (100 mL). The ether layer was decanted and the aqueous phase was extracted with of diethyl ether (3 mL × 70 mL). The combined ether extract was washed with a saturated sodium bisulfite solution (50 mL), washed with water (3 mL × 70 mL), and dried over anhydrous sodium carbonate. The solvent was removed under reduced pressure to give 4 (49.0 g, 86%), as a crude mixture of *cis* and *trans* isomers (30:70 mix from NMR analysis). The mixture of alcohols was then distilled through a fractionating column under reduced pressure to give alcohol mixture 4 (40.5 g, 71%); b.p. 122–127 °C (180 mmHg) (lit.[25] b.p. 119–121 °C @ 164 mmHg); ^{1}H($CDCl_3$) δ 1.68–1.62 (m, 1 H, CH),1.57–0.95 (m, 8 H, CH_2),1.18 (s, 3 H, CH_3), 0.92 (d, 3 H, J = 6.8 Hz, CH_3 *cis*), 0.91 (d, 3 H, J = 6.2 Hz, CH_3 *trans*).

4.3. 1,2-dimethylcyclohexene, 5

A procedure described by Signaigo and Cramer was again employed [25]. The mixture of alcohols 4 (111.3 g, 0.87 mol) was placed in a round-bottomed flask with iodine crystals (0.3 g, 1.18 mmol) and heated. At about 100 °C a reaction initiated and the temperature was adjusted so that the alkene and water distilled slowly over a few hours. The distillate was washed with saturated sodium thiosulfate solution (50 mL) to remove any free iodine and was dried over calcium chloride. The olefin mixture (82.1 g, 86% crude by weight) was then refluxed with sodium (1.0 g, 43.5 mmol) to remove any starting material, and distilled through a fractionating column (90–98 °C @ 220 mmHg) to give 70.1 g (73%) of a mixture of alkenes. Alkene 5 was determined to be 72% of the mixture by NMR analysis and the other components were determined to be 1,6-dimethylcyclohexene (21%) and 2-methylmethylenecyclohexane (7%); ^{1}H($CDCl_3$) δ 1,2-dimethylcyclohexene 1.94–1.90 (m, 4 H, CH_2), 1.65–1.54 (m, 4 H, CH_2),1.60 (s, 6 H, CH_3); 1,6-dimethylcyclohexene 5.4 (*br* s, 1 H, CH), 2.16 (d, 1 H, J = 9.5 Hz, CH) 1.94–1.90 (m, 2 H, CH_2),1.65–1.54 (m, 7 H, 2 × CH_2,1 × CH_3) 1.01 (d, 3 H, J = 7.1, CH_3); 2-methylmethylenecyclohexane 4.6 (*br* d, 2 H, CH_2), 2.26 (*br* s, 1 H, CH), 1.94–1.90 (m, 2 H, CH_2), 1.65–1.54 (m, 6 H, CH_2), 1.03 (d, 3 H, J = 6.4, CH_3).

4.4. trans-1,2-dimethyl-1,2-dinitrocyclohexane, 6

The crude 1,2-dimethylcyclohexene from the previous experiment (10.0 g, 65 mmol of 5 based on composition of the mixture) in dry ether (100 mL) was added dropwise to a stirred solution of dinitrogen tetroxide (25 g, 0.27 mol) in dry ether (200 mL) over a period of 6 h at 0 °C with a slow steam of air bubbling through the reaction mixture. After the addition, the mixture was poured into ice/water (385 mL) and allowed to warm overnight. The organic phase was separated and the solvent was evaporated. The residue was then dissolved in diethyl ether/hexane (1:2, 125 mL) and washed with water (8 mL × 80 mL) until the washings were neutral, dried over anhydrous sodium sulphate, and evaporated to give a green oil (9.5 g, 72% crude). The oil was dissolved in ethanol (25 mL) and added slowly to sodium hydroxide solution (4 M, 195 mL), and the mixture was stirred for 10 h at ambient temperature. The dark red–brown mixture was then extracted with diethyl ether (4 mL × 80 mL), and the combined extracts were dried over sodium sulphate and evaporated to give a cream-yellow solid residue (3.08 g, 23%); ^{1}H($CDCl_3$) δ 1.77 (s, 6 H, CH_3), 1.79 (s), 2.6–1.5 (m, 8 H, CH_2). NMR analysis indicated the presence of a significant impurity (18% of residue from integration) with a signal of 1.79 ppm (s) and this was assumed to be an isomer of the product. The residue was recrystallised from hexane to give 2.05 g (16%) of 6 as a cream-white grainy solid; ^{1}H($CDCl_3$) δ 1.77 (s, 6 H, CH_3), 2.49–1.49 (m, 8 H, CH_2); ^{13}C($CDCl_3$) δ 91.9, 35.4, 22.1, 21.2.

The results of other runs of this reaction are shown in Table 2. The ratio of desired product to the impurity varied considerably but was never more than 50/50. Occasionally, the amount of the impurity was too great (e.g. reaction under oxygen) to be removed by recrystallisation (even three times) so the mixture had to be purified by column chromatography (CH_2Cl_2/pet. spirits; 1:1) but the product yield was then low (0.59 g of pure 6 from 5 g eluted) because of inadequate separation which also frustrated attempts to fully characterise the impurity.

4.5. (±)-trans-1,2-dimethyl-1,2-diaminocyclohexane, rac-3

The procedure of Zhang and Jacobsen [23] was adopted. The dinitro compound 6 (1.42 g, 7.02 mmol) was dissolved in glacial acetic acid (10 mL) and hydrogenated in the presence of $Pd(OH)_2$ on carbon (0.95 g, 20%, 1.35 mmol) under 3 atm of hydrogen for 24 h. The mixture was then filtered and the catalyst washed with ethanol (2 mL × 25 mL). The filtrate and washings were combined, the solvents were removed under vacuum, and the residue was dissolved in water (10 mL) and then sodium hydroxide solution (1.0 M) was added until the solution pH reached 12. The mixture was then extracted with dichloromethane (3 mL × 40 mL). The combined extracts were dried over anhydrous sodium sulphate, and the solvent was removed under vacuum to give (±)-3 as a solidifying colourless oil (0.63 g, 63%); ^{1}H($CDCl_3$) 1.58–1.13 (m, 8 H, CH_2), 1.10 (s, 6 H, CH_3).

4.6. (1R,2R)-1,2-dimethyl-1,2-cyclohexanediammonium bis-(S)-mandelate, (ent)-7

To a solution of (±)-3 (1.86 g, 13.1 mmol) in ethanol (20 mL) was added a solution of (*S*)-(+)-mandelic acid (3.98 g, 26.2 mmol) in ethanol (20 mL) and the mixture was refluxed for 30 min and then cooled to ambient temperature. The solid thus formed (1.70 g) was collected by filtration and the mother liquor retained and set aside. Recrystallisation of the solid four times from ethanol gave pure (*ent*)-7 as white needles (0.48 g, 17% of one diastereomer); $[\alpha]_D = +73.3^\circ$ (c 0.5, H_2O, lit. $[\alpha]_D^{23} = +72.6^\circ$) [23]; ^{1}H($D_2O$) δ 7.35–7.32 (m, 10 H, ArH), 4.92 (s, 2 H, CH), 1.79 (m, 4 H, CH), 1.53 (m, 4 H, CH_2), 1.41 (s, 6 H, CH_3).

4.7. Liberation of (1R,2R)-1,2-dimethyl-1,2-cyclohexanediamine, (R,R)-3

The salt (*ent*)-7 (0.46 g, 1.03 mmol) was treated with NaOH solution (1 M, 8 mL, 8 mmol), and extraction was carried out with dichloromethane (3 mL × 50 mL). The solvent was then evaporated to give (*R,R*)-3 as a white crystalline solid (0.13 g, 90%) which was used immediately in the preparation of salen ligands; ^{1}H ($CDCl_3$) δ 1.59–1.23 (m, 8 H, cyclohexyl), 1.10 (s, 6 H, CH_3).

4.8. (1S,2S)-1,2-dimethyl-1,2-cyclohexanediammonium-bis-(R)-mandelate, (S,S,R,R)-7

The solvent was removed from the initial mother liquor from 4.6 to give an off-white solid (4.14 g) from which the scalemic diamine (0.93 g, 70%) was liberated as *per* 4.7. To a solution of scalemic diamine (0.93 g, 6.5 mmol) in ethanol (10 mL) was added a solution of (*R*)-(−)-mandelic acid (1.98 g, 13 mmol) in ethanol (10 mL) and the mixture was refluxed for 30 min and then cooled to room temperature overnight. After 24 h the crystals (1.29 g) formed were collected by filtration and recrystallised three times from ethanol to give pure (*S,S,R,R*)-7 (0.62 g, 21% of one diastereomer); $[\alpha]_D = -73.3^\circ$ (c 0.5, H_2O); ^{1}H(D_2O) δ 7.35–7.30 (m, 10 H, ArH), 4.90 (s, 2 H, CH), 1.81 (m, 4 H, CH_2), 1.54 (m, 4 H, CH_2), 1.41 (s, 6 H, CH_3); *Anal.* calc. for $C_{24}H_{34}N_2O_2$: C, 64.56; H, 7.68; N, 6.27. Found: C, 64.25; H, 7.55; N, 6.15.

The initial mother liquor from (*S,S,R,R*)-7 was treated in the same way as that from (*ent*)-7 except that (*S*)-mandelic acid was used to prepare the mandelate this time. In this way nearly all of diamine 3 was resolved. The same procedure was applied to the combined recrystallisation filtrates.

4.9. Liberation of (1S,2S)-1,2-dimethyl-1,2-cyclohexanediamine, (S,S)-3

To the salt (*S,S,R,R*)-7 (0.59 g, 1.33 mmol) was added NaOH (1 M, 10 mL, 0.01 mol) and the resulting solution was extracted with dichloromethane (3 mL × 50 mL). The combined organics were then dried over anhydrous sodium sulfate and evaporated to give (*S,S*)-3 (0.17 g, 92%). The diamine was used immediately in the preparation of salen ligands.

4.10. (R,R)-(−)-N,N′-bis(3-trifluoromethane-salicylidene)-trans-1,2-dimethyl-1,2-cyclohexanediamine, 8

(*R,R*)-*trans*-1,2-dimethyl-1,2-cyclohexanediamine *(R,R)*-3 (133 mg, 0.94 mmol) was dissolved in ethanol (50 mL) and 3-trifluoromethanesalicylaldehyde (356 mg, 1.87 mmol) in ethanol (10 mL) was added to the solution. The resulting bright yellow mixture was refluxed for 2 h, cooled and the solvent was removed in vacuo to yield a solid which was recrystallised from hexane to give a yellow powder (377 mg, 83%): m.p. 168–171 °C; $[\alpha]_D = -290^\circ$ (c 0.05, $CHCl_3$); ^{1}H ($CDCl_3$) δ 15.8 (s, 2 H, OH), 8.45 (s, 2 H, imine), 7.63 (d, 2 H, J = 7.6 Hz, ArH), 7.47 (d, 2 H, J = 7.6 Hz, ArH), 6.91 (*app* t, 2 H, J = 7.6 Hz, ArH), 2.17–1.26 (m, 8 H, cyclohexyl), 1.34 (s, 6 H, CH_3); ^{13}C($CDCl_3$) δ 162.0, 161.5, 135.8, 130.3, 124.0 (q, J_{C-F} = 273 Hz), 119.6, 118.5, 117.2, 65.0, 36.5, 21.5, 20.9; ν_{max} (KBr)/cm^{-1}: 2990, 2948, 2869, 2559, 2368, 1633 (C=N), 1497, 1454, 1361, 1332, 1285, 1181, 1135, 1077, 961, 891, 856, 797, 753, 663, 486; m/z (rel. intensity) 486 (M^+, 5), 311 (2), 298 (6), 297 (28), 215 (18), 214 (16), 195 (6), 190 (25); *Anal*. Calc. for $C_{24}H_{24}F_6N_2O_2$: C, 59.26; H, 4.97; N, 5.76; F, 23.43. Found: C, 59.23; H, 4.91; N, 5.99; F, 22.80.

4.11. (S,S)-(+)-N,N′-bis(salicylidene)-trans-1,2-dimethyl-1,2-cyclohexanediamine, 9

(*S,S*)-(+)-1,2-dimethyl-1,2-cyclohexanediamine (*S,S*)-3 (0.17 g, 1.22 mmol) was subjected to reaction with salicylaldehyde (0.30 g, 2.45 mmol) according to the method

of previous section resulting in the formation of a yellow solid which was recrystallised from hexane to give a yellow powder (0.34 g, 80%): m.p. 131–132 °C; $[\alpha]_D = +306°$ (c 0.05, $CHCl_3$); $^1H(CDCl_3)$ δ 14.3 (s, 2 H, OH), 8.44 (s, 2 H, imine), 7.35–7.29 (m, 4 H, ArH), 6.99–6.86 (m, 4 H, ArH), 2.12–2.05 (m, 2 H, cyclohexyl), 1.70–1.62 (m, 6 H, cyclohexyl), 1.26 (s, 6 H, CH_3); $^{13}C(CDCl_3)$ δ 162.0, 161.9, 132.6, 131.9, 119.3, 118.7, 117.4, 64.9, 36.7, 21.7, 20.9; ν_{max} (KBr)/cm^{-1}: 2985, 2940, 2866, 1624, 1579, 1498, 1458, 1441, 1369, 1282, 1273, 1175, 1063, 752; *m*/*z* (rel. intensity) 351 (M + 1, 2), 350 (M^+, 12), 229 (43), 146 (22), 122 (39), 120 (13), 107 (18), 77 (17); *Anal*. Calc. for $C_{22}H_{26}N_2O_2$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.21; H, 7.52; N, 7.91.

4.12. [(R,R)-N,N′-bis(3-trifluoromethanesalicylidene)-1,2-dimethyl-1,2-cyclohexanediamine chromium(III)] chloride hydrate, 10

(*R*,*R*)-(−)-*N*,*N*′-bis(3-trifluoromethanesalicylidene)-*trans*-1,2-dimethyl-1,2-cyclohexanediamine, 8 (0.36 g, 0.73 mmol) and chromium(II) chloride (0.12 g, 0.98 mmol) were subjected to reaction according to the procedure of Jacobsen and co-workers [28] yielding a brown precipitate (0.21 g, 50%) on dilution with *tert*-butyl methyl ether (90 mL); ν_{max} (KBr)/cm^{-1}: 2962, 2893, 2355, 2012, 1625 (C=N), 1600, 1564, 1438, 1398, 1343, 1293, 1191, 1152, 1125, 1076, 965, 857, 766, 640, 554, 491. *Anal*. calc. for $C_{24}H_{26}ClF_6CrN_2O_3$: C, 48.87; H, 3.76; N, 4.75; Cl, 6.01.. Found: C, 47.37; H, 4.05; N, 4.36; Cl, 5.87. Electrospray mass spectrometric analysis: *m*/*z* (rel. intensity) 536.3 (M^+, 100), 553.4 ($M^+ + H_2O$, 70), 568.7 (M^+ + MeOH, 53), 873.2 (76), 1089 ($M^+ \times 2 + H_2O$, 99).

4.13. [(S,S)-N,N′-bis(salicylidene)-1,2-dimethyl-1,2-cyclohexanediamine chromium(III)] chloride hydrate, 11

(*S*,*S*)-(+)-*N*,*N*′-bis(salicylidene)-*trans*-1,2-dimethyl-1,2-cyclohexanediamine, 9 (333 mg, 0.95 mmol) and chromium(II) chloride (0.20 g, 1.63 mmol) were subjected to reaction according to the procedure of Jacobsen and co-workers [28] yielding an initial brown precipitate (11a, 25 mg, 6%): ν_{max} (KBr/cm^{-1}) 2952, 2720, 2466, 1781, 1610, 1578, 1462, 1397, 1339, 1254, 1197, 1107, 769, 569, 482; *Anal*. calcd. for $C_{22}H_{26}ClCrN_2O_3$: C, 58.21; H, 5.77; N, 6.17. Found: C, 52.15; H, 6.58; N, 5.57. On dilution of the filtrate with MTBE another precipitate was obtained (11b, 70 mg, 17%): *Anal* Found: C, 22.52; H, 2.91; N, 2.25. The MTBE extract was worked up to give a brown solid (11c, 167 mg, 40%): ν_{max} (KBr/cm^{-1}) 2954, 2885, 1619, 1547, 1472, 1446, 1395, 1292, 1198, 1151, 844, 762, 464. *Anal*. calc. for $C_{22}H_{26}ClCrN_2O_3$: C, 58.21; H, 5.77; N, 6.17. Found: C, 53.93; H, 5.37; N, 5.94.

4.14. [(R,R)-N,N′-bis(3-trifluoromethanesalicylidene)-1,2-dimethyl-1,2-cyclohexanediamine chromium(III)] nitrate hydrate, 12

[(*R*,*R*)-*N*,*N*′-bis(3-trifluoromethanesalicylidene)-1,2-dimethyl-1,2-cyclohexanediamine chromium(III)]chloride hydrate 10 (198 mg, 0.35 mmol) was dissolved in methanol and a solution of silver nitrate (88 mg, 0.52 mmol) in water was added. The resulting precipitate of silver nitrate was filtered and the filtrate concentrated to yield a brown solid (126 mg, 61%): ν_{max} (KBr/cm^{-1}) 2956, 2894, 2116, 1625, 1562, 1441, 1385, 1344, 1307, 1191, 1125, 860, 757, 720, 643, 554, 510. *Anal*. Calc. for $C_{24}H_{22}F_6CrN_3O_5$: C, 46.76; H, 3.92; N, 6.82; F, 18.49. Found: C, 44.48; H, 3.55; N, 5.98; F, 19.23.

4.15. [(S,S)-N,N′-bis(salicylidene)-1,2-dimethyl-1,2-cyclohexanediamine chromium(III)] hexafluorophosphate hydrate, 13

A solution of potassium hexafluorophosphate (106 mg, 0.58 mmol) in water was added slowly to a solution of [(*S*,*S*)-*N*,*N*′-bis(salicylidene)-1,2-dimethyl-1,2-cyclohexanediamine chromium(III)]chloride hydrate, 11c (167 mg, 0.38 mmol) in methanol. The solution was stirred overnight at ambient temperature and the red-brown solution was then concentrated in vacuo to yield a brown solid 90 mg (43%): ν_{max} (KBr/cm^{-1}) 2945, 2875, 2365, 1618 (C=N), 1547, 1472, 1447, 1393, 1298, 1197, 1151, 906, 843, 747, 557. *Anal*. Calc. for $C_{22}H_{26}CrN_2O_3PF_6$: C, 46.90; H, 4.65; N, 4.97. Found: C, 42.74; H, 4.59; N, 4.52.

4.16. Procedures for analysis of epoxidation reaction product mixtures

Typically the worked up reaction mixture (see below) was dissolved in 1 mL of Et_2O and 1 μL of *n*-decane was added as an internal standard. 1 μL of this solution was then injected onto a GC column. The ee of *trans*-β-methylstyrene oxide was determined with a Supelco cyclodextrin-α capillary column (alphadex 120), 30 m × 0.25 mm i.d., 0.25 μm film operated at an injection temperature of 230 °C and a column temperature of 93 °C, with a column pressure of 18 psi. The ee of *cis*-β-methylstyrene oxide was determined with a Supelco cyclodextrin-β capillary column (betadex 120) 30 m × 0.25 mm i.d., 0.25 μm film. This was operated at an injection temperature of 230 °C and a column temperature of 77 °C with a column pressure of 20 psi. The absolute configuration of *trans*-β-methylstyrene oxide was assigned by comparison of a sample with the data of Witkop and Folz [38] and of Shi and co-workers [39]. The absolute configuration of *cis*-β-methylstyrene oxide was assigned by comparison of the GC retention times to those of a sample made according to the method of Jacobsen et al. [4].

4.17. Epoxidation of E- and Z-β-methylstyrene by the Cr(V)=O derivative of 12 and 13

Iodosylbenzene (1.2 equiv.) was added to a stirred solution of 12 or 13 (30 mg, 1 equiv.) in CH_3CN (5 mL). A deep green/black colour appeared. After stirring for 30 min this solution was filtered and the filtrate cooled to 0 °C using an ice/water bath. Ph_3PO (1 equiv.) was added, followed 5 min later by (*E*)-β-methylstyrene (1 equiv.). The reaction mixture was stirred at 0 °C until the orange-brown colour of the complex returned completely (4–5 h for 12; 9–11 h for 13). The solvent was removed in vacuo and the residue treated with diethyl ether. The diethyl ether washings were flushed through an alumina plug column using diethyl ether as eluant. The eluant was concentrated in vacuo to a small volume (∼1 mL) and this sample was analysed by GC as described above.

4.18. X-ray crystallography

A BRUKER D8 goniometer equipped with a molybdenum X-ray tube and a BRUKER Smart Apex CCD detector was used. Integration was performed by the program SAINT. A semi-empirical absorption correction based on symmetry-equivalent reflections was carried out by the program SADABS. The structure was then solved by direct methods and refined by full-matrix least squares on F^2 using the programs delivered in the SHELXTL-package (SHELXS-97 and SHELXL-97-2). All non-hydrogen atoms were refined using anisotropic thermal parameters. All hydrogen atoms could be located in the difference Fourier map and refined freely using isotropic temperature factors.

(*S*,*S*,*R*,*R*)-7: $C_{24}H_{34}N_2O_6$, $M = 446.53$, orthorhombic, space group $P2_12_12_1$ (#19), with $a = 6.7053(3)$, $b = 18.5440(9)$, $c = 19.0367(9)$ Å, $V = 2367.08(19)$ Å3, $Z = 4$, $D_{(calcd)} = 1.253$ Mg/m3, CCDC 251199 [40].

(*R*,*R*)-8: C_{24} H_{24} N_2 O_2 F_6, $M = 486.45$, hexagonal, space group $P6_1$ (#169), with $a = 11.1135(4)$ Å, $b = 11.1135(4)$ Å, $c = 31.218(3)$ Å, $V = 3339.1(3)$ Å3 $Z = 6$, $D_{(calcd)} = 1.451$ Mg/m3, CCDC 251200 [40].

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References

[1] R.A. Johnson, K.B. Sharpless, I. Ojima (Eds.), Catalytic Asymmetric Synthesis, second ed., Wiley-VCH, New York, 2000, pp. 231–280.
[2] T. Katsuki, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, second ed., Wiley-VCH, New York, 2000, pp. 287–325, Chapter 6B.
[3] E.N. Jacobsen, M.H. Wu, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, vol. II, Springer, New York, 1999, pp. 649–677, Chapter 18.2.
[4] E.N. Jacobsen, W. Zhang, A.R. Muci, J.R. Ecker, L. Deng, J. Am. Chem. Soc. 113 (1991) 7063–7064.
[5] B.D. Brandes, E.N. Jacobsen, J. Org. Chem. 59 (1994) 4378–4380.
[6] C.T. Dalton, K.M. Ryan, V.M. Wall, C. Bousquet, D.G. Gilheany, Top. Catal. 5 (1998) 75–91.
[7] T. Takeda, R. Irie, Y. Shinoda, T. Katsuki, Synlett (1999) 1157–1159.
[8] C. Bousquet, D.G. Gilheany, Tetrahedron Lett. 36 (1995) 7739–7742.
[9] C.T. Dalton, K.M. Ryan, E.J. Coyne, V.M. Wall, C. Bousquet, D.G. Gilheany, Reported as a series of oral presentations at the 211th National meeting of the American Chemical Society, ORGN, New Orleans, 1996, pp. 161–165.
[10] A.M. Daly, M.F. Renehan, D.G. Gilheany, Org. Lett. 3 (2001) 663–666.
[11] A.M. Daly, D.G. Gilheany, Tetrahedron Asymm. 14 (2003) 127–137.
[12] K.M. Ryan, C. Bousquet, D.G. Gilheany, Tetrahedron Lett. 40 (1999) 3613–3616.
[13] A.M. Daly, C.T. Dalton, M.F. Renehan, D.G. Gilheany, Tetrahedron Lett. 40 (1999) 3617–3620.
[14] P. Brandt, P.-O. Norrby, A.M. Daly, D.G. Gilheany, Chem. Eur. J. 8 (2002) 4299–4307.
[15] N.J. Kerrigan, I.J. Langan, C.T. Dalton, A.M. Daly, C. Bousquet, D.G. Gilheany, Tetrahedron Lett. 43 (2002) 2107–2110.
[16] C.P. O'Mahony, E.M. McGarrigle, M.F. Renehan, K.M. Ryan, N.J. Kerrigan, C. Bousquet, D.G. Gilheany, Org. Lett. 3 (2001) 3435–3438.
[17] (a) W. Adam, K.J. Roschmann, C.R. Saha-Moller, D. Seebach, J. Am. Chem. Soc. 124 (2002) 5068;
(b) J.P. Collman, L. Zeng, J.I. Brauman, Inorg. Chem. 43 (2004) 2672;
(c) K.P. Bryliakov, O.A. Kholdeeva, M.P. Vanina, E.P. Talsi, J. Mol. Catal. A 178 (2002) 47;
(d) C. Linde, N. Koliaï, P.-O. Norrby, B. Åkermark, Chem. Eur. J. 8 (2002) 2568;
(e) L. Cavallo, H. Jacobsen, Inorg. Chem. 43 (2004) 2175;
(f) I.V. Khavrutskii, D.G. Musaev, K. Morokuma, J. Am. Chem. Soc. 125 (2003) 13879;
(g) I.V. Khavrutskii, D.G. Musaev, K. Morokuma, Inorg. Chem. 42 (2003) 2606.
[18] H. Shimizu, K. Nakata, T. Katsuki, T. Chem. Lett. (2002) 21080–21081.
[19] P.-O. Norrby, C. Linde, B. Åkermark, J. Am. Chem. Soc. 117 (1995) 11035–11036.
[20] K.N. Houk, N.C. DeMello, K. Condroski, J. Fennen, T. Kasuga, in: H.S. Rzepa, J.P. Snyder, C. Leach (Eds.), Electronic Conference on Heterocyclic Chemistry, ECHET96, London, 24/6-22/7, 1996; (http://www.ch.ic.ac.uk/ectoc/echet96/).
[21] (a) Y.N. Ito, T. Katsuki, Tetrahedron Lett. 39 (39) (1998) 4325–4328;
(b) T. Hamada, T. Fukuda, H. Imanishi, T. Katsuki, Tetrahedron 52 (1996) 515–530;
(c) R. Irie, T. Hashihayata, T. Katsuki, M. Akita, Y. Morooka, Y. Chem. Lett. (1998) 1041–1042.
[22] D.A. Plattner, D. Feichtinger, J. El-Bahraoui, O. Wiest, Int. J. Mass Spectrom. 195/196 (2000) 351–362.
[23] W. Zhang, E.N. Jacobsen, Tetrahedron Lett. 32 (1991) 1711–1714.
[24] A.J. Birch, K.A.M. Walker, Aust. J. Chem. 24 (1971) 513.
[25] F.K. Signaigo, P.L. Cramer, J. Am. Chem. Soc. 55 (1933) 3326–3332.
[26] N.L. Allinger, N.A. Pamphilis, J. Org. Chem. 38 (1973) 316–319.
[27] W.J. Bowyer, D.H. Evans, J. Org. Chem. 53 (1988) 5234–5239.
[28] L.E. Martinez, J.L. Leighton, D.H. Carsten, E.N. Jacobsen, J. Am. Chem. Soc. 117 (1995) 5897–5898.

[29] (a) P. Coggon, A.T. McPhail, F.E. Mabbs, A. Richards, A.S. Thornley, J. Chem. Soc. A (1970) 3296–3303;
(b) M. Bandini, P.G. Cozzi, A. Umani-Ronchi, Chem. Commun. (2002) 919–927.
[30] E.G. Samsel, K. Srinivasan, J.K. Kochi, J. Am. Chem. Soc. 107 (1985) 7606–7617.
[31] (a) H.A. Goodwin, F. Lions, J. Am. Chem. Soc. 82 (1960) 5013–5023;
(b) M.J. O'Connor, B.O. West, Aust. J. Chem. 21 (1968) 369–372.
[32] C.T. Dalton, Ph.D. Thesis, National University of Ireland, 1998.
[33] N. Hosoya, A. Hatakeyama, K. Yanai, H. Fujii, R. Irie, T. Katsuki, Synlett (1993) 641.
[34] (a) J.M. Kerr, C.J. Suckling, P. Bamfield, J. Chem. Soc., Perkin Trans. 1 (1990) 887–895;
(b) E.J. Larson, V.L. Pecoraro, J. Am. Chem. Soc. 113 (1991) 3810–3818;
(c) M.R. Bermejo, A. Castineiras, J.C. Garcia-Monteagudo, M. Rey, A. Sousa, M. Watkinson, C.A. McAuliffe, R.G. Pritchard, R.L. Beddoes, J. Chem. Soc. Dalton Trans. (1996) 2935–2944.
[35] (a) T.L. Sidall, N. Miyaura, J.C. Huffmann, J.K. Kochi, J. Chem. Soc., Chem. Commun. (1983) 1185;
(b) K. Srinivasan, J.K. Kochi, Inorg. Chem. 24 (1985) 4671.
[36] J. Leonard, B. Lygo, G. Procter, Advanced Practical Organic Chemistry, second ed., Blackie, London, 1995.
[37] H. Saltzmann, J.G. Sharefkin, Org. Synth. Coll. 5 (1973) 658–659.
[38] B. Witkop, M. Foltz, J. Am. Chem. Soc. 79 (1957) 197–201.
[39] Y. Tu, Z.-X. Wang, Y. Shi, J. Am. Chem. Soc. 118 (1996) 9806–9807.
[40] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC251199 (salt **7**) and CCDC251200 (ligand **8**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).