Iridium complexes with new 1,2-dithioether chiral ligands containing a rigid cyclic backbone. Application in homogeneous catalytic asymmetric hydrogenation †

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New chiral dithioether compounds (−)-1-benzyl-3,4-bis(methylsulfanyl)pyrrolidine (−)-degusme, (−)-1-benzyl-3,4-bis(isopropylsulfanyl)pyrrolidine (−)-deguspr^i and (+)-1-benzyl-3,4-bis(phenylsulfanyl)pyrrolidine (+)-degusph were prepared from (+)-L-tartaric acid. The addition of the dithioether compounds to a dichloromethane solution of [Ir(cod)$_2$]BF$_4$ afforded the chiral cationic complexes [Ir(cod){(−)-degusme}]BF$_4$ **1** [Ir(cod){(−)-deguspr^i}]BF$_4$·CH$_2$Cl$_2$ **2** and [Ir(cod){(+)-degusph}]BF$_4$ **3**. The dithioether ligands were replaced by PPh$_3$ in complexes **1**, **2** and **3** providing the [Ir(cod)(PPh$_3$)$_2$]BF$_4$ complex. The addition of H$_2$ to **1**, **2** and **3** at −70 °C gave *cis*-dihydridoiridium(III) complexes [IrH$_2$(cod)L]BF$_4$ [L = (−)-degusme **4**, (−)-deguspr^i **5** or (+)-degusph **6**]. The relative stability of possible isomers for complexes **1**–**6** was studied by molecular mechanics calculations. Complexes **1**–**3** were active precursors in the asymmetric hydrogenation of different prochiral dehydroamino acid derivatives and itaconic acid, at room temperature under atmospheric pressure of H$_2$, and the highest enantiomeric excess obtained was 68%.

Introduction

The development of homogeneous catalysis has made considerable progress with the design and synthesis of new chiral phosphines.[1] New complexes of Rh^I, Ir^I and Ru^{II} and a better understanding of their properties have played a fundamental role in revealing the mechanisms of the catalytic process (*e.g.* the hydrogenation of prochiral olefins such as enamides[2] and α,β-unsaturated acids[2,3]).

The synthesis and catalytic activity of organometallic complexes containing sulfur ligands has not been much exploited in spite of having advantages such as lower cost, toxicity and oxidation potential.[4] The synthesis, characterisation and reactivity of rhodium and iridium complexes with new chiral dithioether ligands, that form seven-membered metal chelate rings, BINASMe$_2$,[5] BIPHESMe$_2$[6] and diosR$_2$[7] (R = Me, Pr^i or Ph) have recently been described. The hydroformylation of styrene with rhodium complexes of the dithioether BINASMe$_2$,[5a,6] BIPHESR$_2$[6] (R = Me or Pr^i), diosR$_2$[7b] (R = Me or Pr^i) takes place with high catalytic activity, but the enantiomeric excesses (e.e.s) obtained are quite low. The iridium complexes of the diosR$_2$ ligands are also able efficiently to catalyse the hydrogenation of acrylic acids. However the enantiomeric excesses obtained are always lower than 47%.[7a] The interconversion through conformational equilibration of the chelate ring achieved with the dithioether ligands that form seven-membered chelate rings could be one of the reasons for the low enantiomeric excess.[5b] Thus, the structure of the ligand backbone and the size of the metal chelate ring proved to be determining factors in the efficiency and stereoselectivity of the catalytic transfer hydrogenation reactions of acrylic acids.[8] Chiral diphosphines that form a five-membered metal chelate ring, *e.g.* Deguphos with a rigid backbone and the chiral centre

closer to the metal, considerably improved the reaction stereoselectivity (the e.e. was as high as 90%[9]) in comparison with DIOP derivatives which form seven-membered chelates.

BINASMe$_2$ BIPHESR$_2$ R=Me, Pr^i diosR$_2$ R= Me, Pr^i, Ph

Deguphos   DIOP
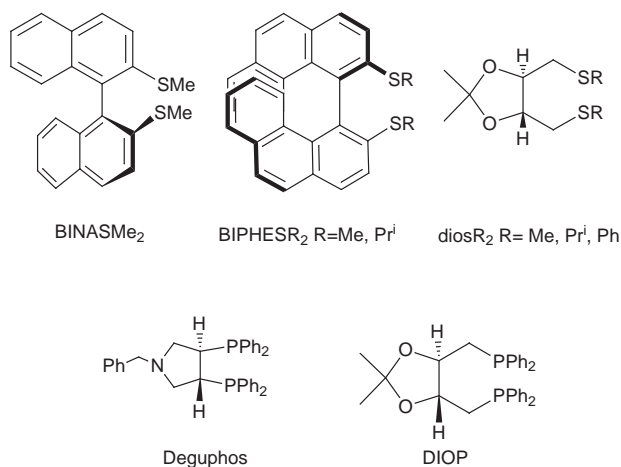
In this paper we describe the synthesis of three new chiral dithioethers with a rigid cyclic backbone, (−)-degusme, (−)-deguspr^i and (+)-degusph. The new iridium complexes in which the chiral ligands form a five-membered ring with the metal center have been isolated and their structure and reactivity are discussed. They have proved to be active in the asymmetric hydrogenation of prochiral acrylic acids, giving 68% e.e. in the reduction of itaconic acid (methylenebutanedioic acid). To the best of our knowledge this is the highest e.e. reported using metal chiral dithioether complexes.

Results and discussion

Synthesis of the dithioether

The new compounds (−)-degusme, (−)-deguspr^i and (+)-

Table 1 The NMR spectroscopic data for the dithioethers[a]

Compound	CH$_2$Ph	CH$_2$N	CH	SMe	SCH	Me	Ph
^{1}H							
(−)-degusme	3.55 (d)[b] 3.65 (d)	2.55 (m) 3.12 (m)	3.05 (m)	2.15 (s)	—	—	7.30 (m)
(−)-deguspr^i	3.60 (d)[c] 3.62 (d)	2.55 (m) 3.02 (m)	3.20 (m)	—	3.01 (m)	1.26 (d)[d] 1.27 (d)[d]	7.30 (m)
(+)-degusph	3.65[e] 3.77 (d)	2.71 (m) 3.21 (m)	3.65 (m)	—	—	—	7.10–7.30 (m)
^{13}C							
(−)-degusme	59.6	60.1	50.4	14.9	—	—	127.0, 128.2 128.5, 138.4
(−)-deguspr^i	59.6	61.3	48.5	—	35.5	23.7 23.8	126.9, 128.2 128.6, 138.8
(+)-degusph	59.5	59.3	51.7	—	—	—	126.8, 127.0 128.2, 128.5 128.9, 131.1 135.2, 138.3

[a] In CDCl$_3$. Chemical shifts δ in ppm with SiMe$_4$ as internal standard, coupling constants in Hz; room temperature. Abbreviations: s, singlet; m, multiplet; d, doublet. [b] $^2J_{HH}$ = 15 Hz. [c] $^2J_{HH}$ = 11.5 Hz. [d] $^3J_{HH}$ = 7.2 Hz. [e] $^2J_{HH}$ = 13.1 Hz.
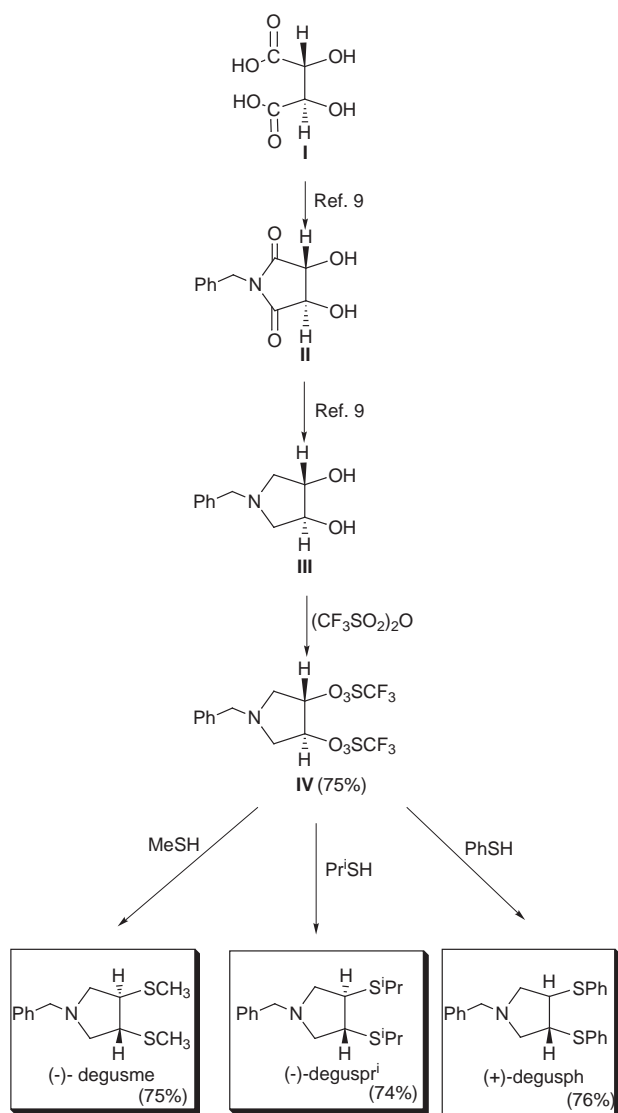
Scheme 1 Synthetic procedures for the preparation of (−)-degusme, (−)-deguspr^i and (+)-degusph.

degusph were prepared from (+)-L-tartaric acid **I** (Scheme 1). Compounds **II** and **III** have been described in the literature.[9] The diol **III** was converted into the ditriflate **IV** by adding pyridine and triflic anhydride to a dichloromethane solution of

III. The ditriflate was isolated as a white solid and characterised by elemental analysis and ^{1}H and ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum shows a quadruplet at δ 118.2 ($^1J_{CF}$ = 321 Hz) which confirms the presence of a triflate group. Compound **IV** is stable in air at low temperature. Treatment of compound **IV** with NaH and methanethiol, propane-2-thiol or benzenethiol in tetrahydrofuran (thf) affords (−)-degusme, (−)-deguspr^i and (+)-degusph, respectively. The (−)-degusme and (−)-deguspr^i were isolated as colourless liquids and they were not stable in air at room temperature but at low temperature were stable for several days. The (+)-degusph was isolated as a white solid stable in air at room temperature.

The dithioethers were characterised by elemental analysis and ^{1}H, ^{13}C NMR spectroscopy. The NMR signals for (−)-deguspr^i and (+)-degusph were assigned using correlation spectroscopy (COSY) and heteronuclear correlation spectroscopy (HETCOR). The chemical shifts and coupling constants are listed in Table 1. The diastereotopic methylenic protons CH$_2$Ph appear as two doublets in all cases. The four methylenic protons CH$_2$N appear as two multiplet signals and in ^{13}C NMR spectra only one signal is observed for these secondary carbon atoms for all compounds. The ^{1}H and ^{13}C NMR spectra also show only one signal for the methinic protons CH and tertiary carbon atoms for the three compounds. The two Me, Pr^i and Ph groups bonded to each sulfur atom are equivalent. A C_2 symmetry seems to be observed in all cases. This suggests that the CH$_2$Ph group rotates freely, as predicted by a molecular mechanics calculation.

Synthesis of the dithioether complexes [Ir(cod){(−)-degusme}]-BF$_4$ 1, [Ir(cod){(−)-deguspr^i}]BF$_4$·CH$_2$Cl$_2$ 2 and [Ir(cod){(+)-degusph}]BF$_4$ 3

The reaction of the corresponding chiral dithioether degusR (R = Me, Pr^i or Ph) with [Ir(cod)$_2$]BF$_4$ in dichloromethane solution proceeded with the displacement of one cycloocta-1,5-diene ligand to afford the cationic complexes **1**, **2** and **3** (Scheme 2). The complexes were isolated by adding diethyl ether as yellow (**1** and **3**) and orange (**2**) moderately air-stable powders. The elemental analysis of C, H and S matches the stoichiometry [{Ir(cod)(degusR)}]$_n$[BF$_4$]$_n$ for **1** and **3** and [{Ir(cod)(degusR)}]$_n$[BF$_4$]$_n$·nCH$_2$Cl$_2$ for **2**. The FAB mass spectra show the ions at m/z 554 **1**, 610 **2** and 678 **3** which correspond to the loss of the BF$_4^-$ anion in the molecular species. For complex **2**, CH$_2$Cl$_2$ is also lost. These peaks are accompanied by peaks at +16 (m/z 570 **1**, 626 **2**, 694 **3**) and +32 mass units (m/z 586 **1**, 642 **2**, 710 **3**). It is probable that all these peaks
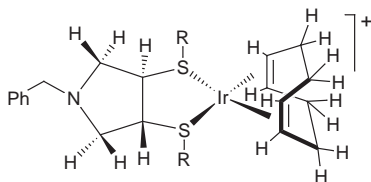
Fig. 1 Molecular symmetry of the cationic complexes [Ir(cod)-(degusR)]$^+$.
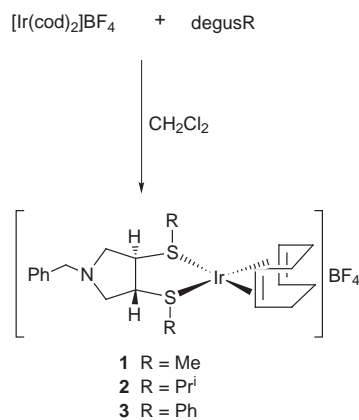

Scheme 2

correspond to the addition of one and two oxygen atoms from the matrix to the mononuclear complexes.[10] The IR spectra show a strong band between 1090 and 1050 cm^{-1} and a medium band around 450 cm^{-1} for all complexes which are characteristic of the non-co-ordinated BF$_4^-$ anion in cationic complexes.[11] Complex **1** is unstable in solution even under a nitrogen atmosphere and it could only be characterised in the solid state. The ^{1}H NMR data for complexes **2** and **3** were assigned using COSY spectra.

When the chiral dithioethers (−)deguspr^i and (+)-degusph were co-ordinated to iridium–cyclooctadiene fragments a C_2 symmetry seemed to be observed in cationic complexes **2** and **3** (Fig. 1). In this way the ^{1}H NMR spectra show the olefinic proton signals of the co-ordinated cyclooctadiene ligand as two multiplets. For the *endo-* and *exo-*methylenic protons of cyclooctadiene four signals were observed for complex **3** and three for **2**. For the signals from the dithioether ligand, the four diastereotopic methylenic protons CH$_2$N appear as an ABX system showing two multiplets and the two methinic protons CH as one multiplet. In complex **2** the two Pr^{i}S groups are equivalent, so diastereotopic methyl protons appear as two doublets at δ 1.50 and 1.60 ($^3J_{HH}$ = 6.3 Hz) and the methinic protons as one multiplet. For complex **3** the aromatic protons of the PhS and CH$_2$Ph groups are very close together and they could not be separated sufficiently to be reliably determined.

A feature of dithioether ligands is that upon co-ordination they can give rise to different diastereomeric complexes, since the two sulfur donors become stereogenic centers. Since the chiral dithioether ligands degusR have a (*R,R*) configuration, there are three possible diastereomers with the configurations *RRSS*, *RRRR* and *RRRS* or *RRSR* (Fig. 2). The diastereomers *RRSS* and *RRRR* correspond to the *anti* invertomer and the *RRRS* or *RRSR* to the *syn*.[12] If the CH$_2$Ph group rotates freely the diastereomers *RRSS* and *RRRR* present a C_2-geometry. All the NMR data indicate that only one of the two possible *anti* diastereomers can be distinguished for complexes **2** and **3** or the interconversion among them is fast on the NMR timescale at room temperature. When the temperature was changed from −70 to 75 °C no other signals were observed in the ^{1}H NMR spectra. Similar behaviour has been observed for the related complexes [Ir(cod)L]BF$_4$[7a] [L = (−)-diosme, (−)-2,2-dimethyl-4,5-bis(methylsulfanylmethyl)-1,3-dioxolane; (−)-diospr^i, (−)-4,5-bis(isopropylsulfanylmethyl)-2,2-dimethyl-
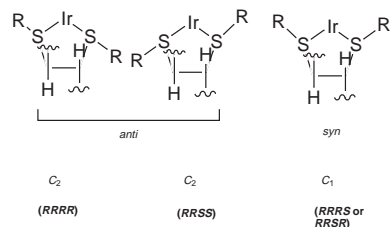
Fig. 2 The three possible diastereomers expected for complexes [Ir(cod)(degusR)]$^+$.

1,3-dioxolane; or (+)-diosph, (+)-2,2-dimethyl-4,5-bis(phenyl-sulfanylmethyl)-1,3-dioxolane] and [Rh(cod)L]ClO$_4$[7b] [L = (−)-diosme or (−)-diospr^i].

In order to determine the relative stability of the three possible diastereomers, molecular mechanics calculations were carried out. From the relative strain energies obtained for the three possible diastereomers for complexes **1**, **2** and **3** it can be concluded that for **2** and **3** the most stable diastereomer is the *anti* with the configuration *RRSS*. These results correlate well with experimental NMR data and suggest that no interconversion between *anti* diastereomers takes place on the NMR timescale at room temperature. For complex **1** no significant energy differences between the *anti RRSS* and *syn* diastereomers have been observed. The molecular mechanics calculation also indicates that the CH$_2$Ph group freely rotates which is in accord with the C_2 symmetry observed by ^{1}H NMR. Minimised structures of the three possible diastereoisomers of complex **2** are available as supplementary material (SUP 57426).

Reactivity of olefinic complexes

With PPh$_3$. The reaction of the diene complexes [Ir(cod)-(degusR)]BF$_4$ (R = Me **1**, Pr^i **2** or Ph **3**) with PPh$_3$ in a complex:PPh$_3$ molar ratio of 1:2 results in displacement of the dithioether ligands and provides the previously prepared complex [Ir(cod)(PPh$_3$)$_2$]BF$_4$.[11]

With H$_2$. When H$_2$ is bubbled for 30 min at −70 °C and at atmospheric pressure through CD$_2$Cl$_2$ solutions of olefinic iridium complexes **1**, **2** and **3** the *cis*-dihydrido olefin complexes **4**, **5** and **6** are formed in solution (Scheme 3). In the high-field region of the ^{1}H NMR spectrum of the CD$_2$Cl$_2$ solution of all complexes at −70 °C four signals of two different intensities can be observed at δ −12.51, −13.43 and −12.94 and −13.74 (relation 2:1) for **4**, at δ −13.10, −13.67 and −12.54 and −14.19 (relation 9:1) for **5** and at δ −9.85, −13.30 and −10.69 and −13.79 (relation 10:1) for **6**. These signals may be from two diastereomeric dihydridoiridium complexes in each case. In a CD$_2$Cl$_2$ solution of the related complex *cis*-[IrH$_2$(cod){(−)-diospr^i}]BF$_4$[7a] two possible diastereomers were also distinguished. In the low-field region of the ^{1}H NMR spectra for the CD$_2$Cl$_2$ solutions of **4**, **5** and **6** there are signals corresponding to co-ordinated cyclooctadiene and dithioether, together with starting material. The Fourier-transform IR spectrum in CD$_2$Cl$_2$ solution at −70 °C of **4**, **5** and **6** shows two asymmetric absorption bands, ν(Ir–H) between 2000 and 2094 cm^{-1}, which are expected for *cis*-dihydroiridium(III) compounds.[13] Only the major diastereomer is observed in all the cases.

When the temperature is increased to −40 °C hydrogen is lost and the parent complexes are recovered. This indicates that the equilibrium of the dihydridoiridium complexes in solution with the parent complexes depends on the temperature (Scheme 3). The related olefinic dihydrido complexes *cis*-[IrH$_2$(cod)L]BF$_4$ [L = (−)-diosme, (−)-diospr^i or (+)-diosph][7a] and *cis*-[IrH$_2$-(cod)L$_2$]PF$_6$ (L = PMePh$_2$, PPh$_3$, $\frac{1}{2}$dppe, PBu$^n_3$ or $\frac{1}{2}$DIOP) also behave similarly[14] but hydrogen is lost on warming to 25 °C. The hydride resonances have T_1 values around 400 ms for all complexes, in CD$_2$Cl$_2$ at −70 °C and 300 MHz. These values are consistent with classical hydride.[15]
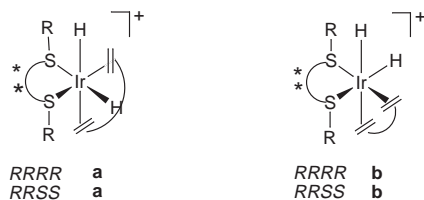
Fig. 3 The four possible *anti* isomers of complexes *cis*-[IrH₂(cod)-(degusR)]⁺.

$$\text{Fig. 3: } cis\text{-[IrH}_2\text{(cod)(degusR)]}^+$$

Scheme 3
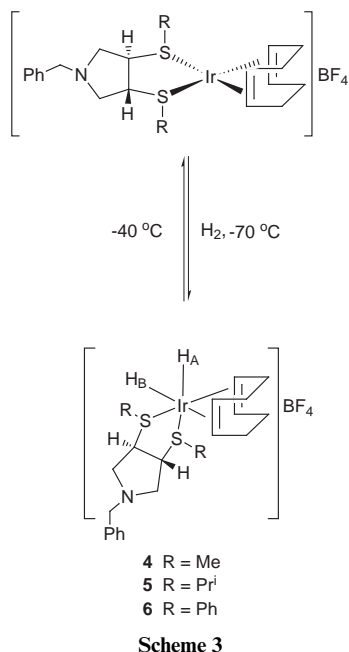
When diethyl ether is added to a CH₂Cl₂ solution of *cis*-[IrH₂(cod){(+)-degusph}]BF₄ **6** at −70 °C a light yellow powder is obtained. The Fourier-transform IR spectrum in KBr shows a very broad signal at 2003 cm⁻¹ which may include the two asymmetric absorption bands, ν(Ir–H), expected. The situation is similar for the related complexes *cis*-[IrH₂(cod)-{(−)-diosme}]BF₄[7a] and *cis*-[IrH₂(cod)(dth)]ClO₄ (dth = 2,6-dithiaheptane).[16]

Molecular mechanics calculations were carried out for dihydride complexes **4**, **5** and **6**. The dihydride complexes can be present in eight different possible isomers, however this study has shown that due to the steric hindrance the number is reduced to the four *anti* isomers (Fig. 3). The relative strain energies for these indicate that the two most stable isomers are **a**. For complexes **5** and **6** the most stable isomer in solution has the *anti RRSS* configuration of the dithioether. In the case of **4** there is no significant energy difference between the two isomers **a**. In all cases, the difference obtained in the calculated strain energies between the two isomers **a** correlates well with the relative abundance of these isomers observed by ¹H NMR. Minimised structures for compound **4** are available as supplementary material (SUP 57426).

Catalytic activity

Asymmetric hydrogenation of prochiral olefins. It has been previously reported that cationic complexes containing chiral dithioether ligands behave as catalyst precursors in asymmetric hydrogenation[7a] and hydroformylation[5a,6,7b] without the addition of phosphorus ligands. In this work the mononuclear cationic iridium complexes **1**–**3** were initially used as catalyst precursors in the asymmetric hydrogenation of prochiral olefins Z-α-(acetamido)cinnamic acid **V**, α-(acetamido)acrylic acid **VI** and itaconic acid (methylenebutanedioic acid) **VII** at room temperature under atmospheric pressure of H₂.

The conversion and enantioselectivity results are shown in

Table 2 Hydrogenation results with catalytic systems **1**–**3** and **7**[a]

Entry	Precursor	Substrate	t/h	Conversion (%)	e.e. (%)
1	**1**	**V**	16	60	2(S)
2	**2**	**V**	3	100	2(S)
3	**3**	**V**	3	100	20(S)
4	**2**	**VI**	2	96	10(R)
5	**3**	**VI**	2	100	27(R)
6	**2**	**VII**	2	100	35(R)[b]
7	**3**	**VII**	2.5	100	68(R)[b]
8	**7**	**V**	6	96	—
9	**7**	**VI**	6	100	—
10	**7**	**VII**	6	98	—

[a] At 20 °C and 1 atm H₂. Solvent 6 ml, CH₂Cl₂. Substrate : precursor = 40 : 1. [b] Determined by polarimetry.
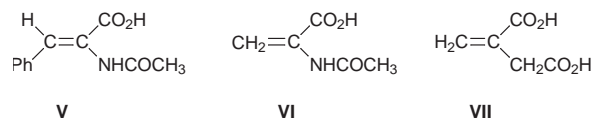

Table 2. It can be seen, that the iridium complexes **1**, **2** and **3** all lead to active hydrogenation systems. However **2** and **3** are more efficient (entries 2, 3) than **1** (entry 1). The hydrogenation of **V** with the catalytic systems **2** and **3** is completed in 3 h although the e.e. is low (entries 2 and 3). For hydrogenation of compounds **VI** (entries 4, 5) and **VII** (entries 6, 7) the activity of catalytic systems **2** and **3** is similar, but the e.e. is higher for precursor **3**. Thus the e.e. is highest when compound **VII** is hydrogenated with precursor **3** (68% R).

For comparative purposes, experiments using [Ir(cod)₂]BF₄ **7** without a chiral dithioether ligand were carried out, giving lower activities (entries 8, 9 and 10). This, together with the enantioselectivity obtained in all cases, indicates that the active species for precursors **1**, **2** and **3** are modified by the chiral dithioether ligand.

In general, although catalytic systems **1**, **2** and **3** are active under ambient conditions of pressure and temperature, the e.e.s are low. The higher e.e. obtained with catalytic system **3** could be due to the phenyl ring bonded to sulfur facilitating the transmission of chirality from the dithioether ligand.

The catalytic sytems **1**, **2** and **3** in which the chiral ligands form a five-membered ring with the metal center are more active and **3** more enantioselective than the related seven-membered ring iridium–chiral dithioether (−)-diosme, (−)-diospr[i] and (+)-diosph systems previously reported[7a] for the asymmetric hydrogenation of the prochiral olefins cited. It should be noted that the absolute configuration obtained with systems **1**, **2** and **3** is opposite to the one obtained with the related diosR₂ (R = Me, Pr[i] or Ph) for the hydrogenation of compounds **V**–**VII**.[7a]

Experimental

General comments

Elemental analyses were carried out with a Carlo-Erba microanalyzer. Infrared spectra were recorded on a Midac Grams/386 spectrophotometer, ¹H and ¹³C NMR spectra on a Varian Gemini 300 MHz spectrometer. Proton T_1 studies were performed using the standard inversion recovery 180°–τ–90° pulse sequence method.[15a] The FAB mass spectrometry was performed on a VG autospect in a 3-nitrobenzyl alcohol matrix. Gas chromatography analyses were performed in a Hewlett-Packard 5890A instrument (fused silica capillary column 25 m × 0.25 mm permabond L-Chirasil-Val). Optical rotations were determined with a Perkin-Elmer 241 MC polarimeter.‡ All

‡ Specific rotations (at the temperature indicated) are given in ° cm³ g⁻¹ dm⁻¹ with the concentration of the solution expressed in 10⁻² g cm⁻³.

iridium complexes and ligands were synthesized under nitrogen using standard Schlenk techniques. Solvents were distilled and deoxygenated before use. The iridium compound [Ir(cod)₂]-BF₄[11] was prepared by the general procedures described.

Computational details

The molecular mechanics calculations were made using the program CERIUS 2[17] with the force field UFF developed by Rappe and co-workers.[18] Electrostatic interations were taken into account from atomic charges generated by the Qeq method.[19]

Ligand synthesis

(−)-1-Benzyl-3,4-bis(methylsulfanyl)pyrrolidine, (−)-degusme. A suspension of NaH (0.83 g, 34 mmol) in paraffin, cleaned twice in hexane, in thf (16 ml) was cooled to −78 °C and methanethiol (0.5 ml, 9 mmol) at −78 °C added. The resulting solution was stirred and the temperature increased to 0 °C. After 5 min the solution was cooled and compound **IV** (0.5 g, 1.1 mmol) in thf (5 ml) added. After 45 min the solvent was evaporated and water (100 ml) added to the residue and extracted with dichloromethane (3 × 50 ml). The extract was then dried and concentrated. The residue was purified by column chromatography (hexane–ethyl acetate, 5:1) and degusme was obtained (0.2 g, 75%) as a colourless liquid: $[\alpha]_D^{23} = -19.9$ (c 0.55 in CHCl₃) (Found: C, 61.94; H, 7.93; N, 5.66; S, 25.33. Calc. for C₁₃H₁₉NS₂: C, 61.61; H, 7.56; N, 5.53; S, 25.30%).

(−)-1-Benzyl-3,4-bis(isopropylsulfanyl)pyrrolidine, (−)-deguspr^i. A solution of propane-2-thiol (0.52 ml, 5.6 mmol) in thf (8 ml) was added to a suspension of NaH (0.56 g, 23.3 mmol) in paraffin, cleaned twice in hexane, in thf (1 ml). The resulting solution was stirred for 20 min. Then compound **IV** (0.9 g, 2.0 mmol) in thf (9 ml) was added. After 45 min the solvent was evaporated and 50 ml of water were added to the residue and extracted with dichloromethane (3 × 50 ml). The extract was then dried and concentrated. The residue was purified by column chromatography (hexane–ethyl acetate, 20:1) and deguspr^i was obtained (0.4 g, 74%) as a colourless liquid: $[\alpha]_D^{23} = -24.5$ (c 0.55 in CHCl₃) (Found: C, 65.38; H, 8.96; N, 4.65; S, 20.32. Calc. for C₁₇H₂₇NS₂: C, 65.97; H, 8.79; N, 4.65; S, 20.72%).

(+)-1-Benzyl-1,4-bis(phenylsulfanyl)pyrrolidine, (+)-degusph. A solution of benzenethiol (0.50 ml, 4.9 mmol) in thf (6 ml) was added to a suspension of NaH (0.62 g, 25.8 mmol) in paraffin, cleaned twice in hexane, in thf (1 ml). The resulting solution was stirred for 20 min. Then compound **IV** (0.8 g, 1.76 mmol) in thf (9 ml) was added. After 45 min the solvent was evaporated and 50 ml of water were added to the residue and extracted with dichloromethane (3 × 50 ml). The extract was then dried and concentrated. The residue was purified by column chromatography (hexane–ethyl acetate, 20:1) and degusph was obtained (0.5 g, 76%) as a white solid: $[\alpha]_D^{23} = +52.7$ (c 0.55 in CHCl₃) (Found: C, 73.53; H, 6.23; N, 3.69; S, 16.99. Calc.for C₂₃H₂₃NS₂: C, 73.17; H, 6.14; N, 3.71; S, 16.98%).

(S,S)-1-Benzyl-3,4-bis(trifluoromethylsulfanyloxy)pyrrolidine IV. Pyridine (0.56 ml, 7.0 mmol) was added to a solution of compound **III** (0.5 g, 2.6 mmol) in dichloromethane (18.5 ml). The resulting solution was stirred for 10 min. Then it was cooled to −20 °C and triflic anhydride (1 ml, 6.1 mmol) slowly added. TLC Monitoring of the reaction showed that it was complete after 25 min (hexane–ethyl acetate, 3:2). The solvents were evaporated under vacuum and the residue was purified by column chromatography (hexane–ethyl acetate, 5:1). White solid (0.9 g, 75%), $[\alpha]_D^{23} = -42.0$ (c 3.2 in CHCl₃) (Found: C,

34.15; H, 2.91; N, 3.12; S, 13.96. Calc. for C₁₃H₁₃F₆NO₆S₂: C, 34.14; H, 2.86; N, 3.06; S, 14.02%). δ_H(300 MHz, CDCl₃, SiMe₄) 2.85 (2 H, m, CH₂N), 3.20 (2 H, m, CH₂N), 3.70 (2 H, m, CH₂Ph), 5.35 (2 H, m, CH) and 7.30 (5 H, m, Ph). δ_C(74.5 MHz, CDCl₃) 57.2 (CH₂N), 58.6 (CH₂Ph), 87.8 (CH₂N), 118.2 (q, CF₃, J_{CF} = 320.2 Hz), 127.9, 128.5 and 128.7 (CH, Ph) and 136.1 (C, Ph).

Synthesis of the complexes

[Ir(cod){(−)-degusme}]BF₄ 1. The compound was prepared by adding an excess of (−)-degusme (20 mg, 0.1 mmol) to a dichloromethane solution of [Ir(cod)₂]BF₄ (40 mg, 0.08 mmol) which produced an immediate colour change from brown-red to orange. Subsequent addition of diethyl ether precipitated the desired complex, which was filtered off, washed with cold ether, and vacuum dried. Yield 46.5 mg, 90% (Found: C, 38.94; H, 5.03; N, 2.22; S, 9.82. Calc. for C₂₁H₃BF₄IrNS₂: C, 39.37; H, 4.87; N, 2.19; S, 10.00%). m/z 554 (M⁺).

[Ir(cod){(−)-deguspr^i}]BF₄·CH₂Cl₂ 2. The compound was prepared by adding an excess of (−)-deguspr^i (25 mg, 0.1 mmol) to a dichloromethane solution of [Ir(cod)₂]BF₄ (40 mg, 0.08 mmol) which immediately caused a colour change from brown-red to orange. Subsequent addition of ether precipitated the desired complex **2**, which was filtered off, washed with cold ether and vacuum dried (46.0 mg, 81%) (Found: C, 39.19; H, 5.78; N, 1.80; S, 8.16. Calc. for C₂₅H₃BF₄IrNS₂: C, 39.95; H, 5.20; N, 1.79; S, 8.20%). m/z 610 (M⁺) δ_H(300 MHz, CDCl₃, SiMe₄) 1.50 (6 H, d, J_{HH} = 6.3, Me) and 1.60 (6 H, d, J_{HH} = 6.3, Me), 2.15 (2 H, m, CH₂, cod), 2.25 (2 H, m, CH₂, cod), 2.45 (4 H, m, CH₂, cod), 3.15 (2 H, m CH₂N), 3.35 (2 H, m CH₂N), 3.35 (2 H, m, CH), 3.85 (1 H, m, CH₂Ph), 4.05 (2 H, m, SCH), 4.10 (1 H, m, CH₂Ph), 4.40 (2 H, m, CH, cod), 4.60 (2 H, m, CH, cod), 5.32 (2 H, s, CH₂Cl₂) and 7.40 (5 H, m, Ph).

[Ir(cod){(+)-degusph}]BF₄ 3. The compound was prepared by adding an excess of (+)-degusph (30 mg, 0.1 mmol) to a dichloromethane solution of [Ir(cod)₂]BF₄ (40 mg, 0.08 mmol) which caused an immediate colour change from brown-red to yellow. Subsequent addition of ether precipitated the desired complex **3**, which was filtered off, washed with cold ether, and vacuum dried (61.0 mg, 98%) (Found: C, 48.72; H, 5.19; N, 1.72; S, 8.16. Calc. for C₃₁H₃₅BF₄IrNS₂: C, 48.69; H, 4.61; N, 1.83; S, 8.38%). m/z 678 (M⁺) δ_H(300 MHz, CDCl₃, SiMe₄) 1.50 (2 H, m, CH₂, cod), 2.10 (2 H, m, CH₂, cod), 2.20 (2 H, m, CH₂, cod), 2.60 (2 H, m, CH₂, cod), 2.80 (2 H, m, CH₂N), 2.85 (1 H, m, CH₂Ph), 3.30 (2 H, m, CH₂N), 3.80 (2 H, m, CH), 4.00 (1 H, m, CH₂Ph), 4.50 (2 H, m, CH, cod) and 4.80 (2 H, m, CH, cod) and 7.30–7.90 (15 H, m, Ph).

[IrH₂(cod){(−)-degusme}]BF₄ 4. Hydrogen was bubbled through a yellow solution of [Ir(cod){(−)-degusme}]BF₄ (40 mg, 0.062 mmol) in CD₂Cl₂ (0.4 ml) at −70 °C for 30 min. The compound was then transferred to an NMR spectrometer tube and the ¹H spectrum recorded (see text for ¹H NMR data and characterisation).

[IrH₂(cod){(−)-deguspr^i}]BF₄ 5. Hydrogen was bubbled through a brown-orange solution of [Ir(cod){(−)-deguspr^i}]-BF₄ (40 mg, 0.057 mmol) in CD₂Cl₂ (0.4 ml) at −70 °C for 30 minutes. The compound was then transferred to an NMR spectrometer tube and the ¹H spectrum recorded (see text for ¹H NMR data and characterisation).

[IrH₂(cod){(+)-degusph}]BF₄ 6. Hydrogen was bubbled through a yellow solution of [Ir(cod){(−)-deguspr^i}]BF₄ (40 mg, 0.052 mmol) in CD₂Cl₂ (0.4 ml) at −70 °C for 30 min. By adding diethyl ether at −70 °C a yellow powder **6** was obtained (Found: C, 48.01; H, 5.00; N, 1.82; S, 8.44. Calc. for C₃₁H₃₈-

BF$_4$IrNS$_2$: C, 48.00; H, 4.90; N, 1.82; S, 8.46%); see text for ^{1}H NMR data and characterisation: $\tilde{\nu}_{max}$/cm^{-1} (Ir–H) 2003 (br).

Catalytic hydrogenations

The reactions under 1 atm of H$_2$ were performed in a previously described hydrogen-vacuum line.[20] In a typical run, substrate (100 mg) and catalyst precursor (2.5 mg), dissolved in dichloromethane (6 ml), were shaken under H$_2$ (1 atm) at 293 K. After the required time (see Table 2), the solvent was removed. The conversion was measured by ^{1}H NMR.

Work-up of the hydrogenation product. The following procedures were used to isolate the hydrogenation product. A, For *N*-acetylalanine, the residue was dissolved in water and separated from the insoluble catalyst by filtration; evaporation to dryness afforded the product. B, For methylsuccinic acid and *N*-acetylphenylalanine, the residue was dissolved in 0.5 mol dm^{-3} NaOH and separated from the insoluble catalyst by filtration. The filtrate was acidified with dilute HCl, extracted with ether, and washed with a little water. The ether phase was dried over sodium sulfate and evaporated to dryness. C, For *N*-acetylphenylalanine and *N*-acetylalanine, gas chromatography analyses were performed in a Hewlett-Packard 5890A instrument (fused silica capillary column 25 m × 0.25 mm permabond L-Chirasil-Val) before treating the sample as described.[21]

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