DALTON
FULL PAPER

Iridium complexes containing the first sugar dithioether ligands. Application as catalyst precursors in asymmetric hydrogenation

Oscar Pàmies, Montserrat Diéguez, Gemma Net,* Aurora Ruiz* and Carmen Claver

Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Pl. Imperial Tàrraco 1, 43005 Tarragona, Spain. E-mail: aruiz@quimica.urv.es

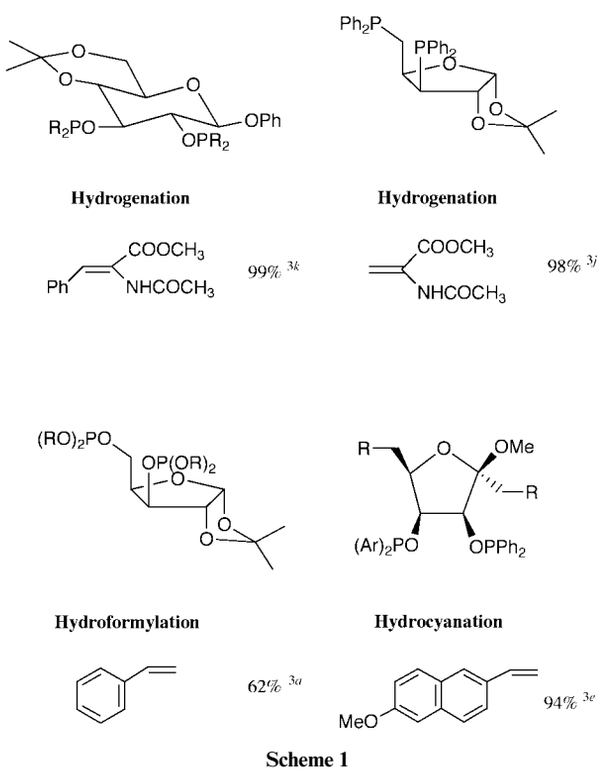
Received 5th July 1999, Accepted 4th August 1999

The first family of sugar derivative dithioethers 1,2-*O*-isopropylidene-3,5-bis(methylsulfanyl)-, (+)-RiSSMe$_2$, 1,2-*O*-isopropylidene-3,5-bis(isopropylsulfanyl)-, (+)-RiSSPr$^i_2$, and 1,2-*O*-isopropylidene-3,5-bis(phenylsulfanyl)-α-D-(+)-ribofuranose, (+)-RiSSPh$_2$, was prepared from 1,2-*O*-isopropylidene-3,5-di-*O*-trifluoromethanesulfonyl-D-xylofuranose. Reaction of these chiral C_1 symmetrical dithioether ligands with [Ir(cod)$_2$]BF$_4$ (cod = 1,5-cyclooctadiene) yielded the iridium complexes [Ir(cod){(+)-RiSSR$_2$}]BF$_4$ **1**–**3**. Their reaction with H_2 at 0 °C gave the *cis*-dihydrido-iridium(III) complexes [IrH$_2$(cod){(+)-RiSSR$_2$}]BF$_4$ **4**–**6**. Complexes **1**–**3** were tested in the asymmetric hydrogenation of acrylic acid derivatives at 1 bar of H_2 and room temperature, providing enantioselectivities of up to 62%.

Introduction

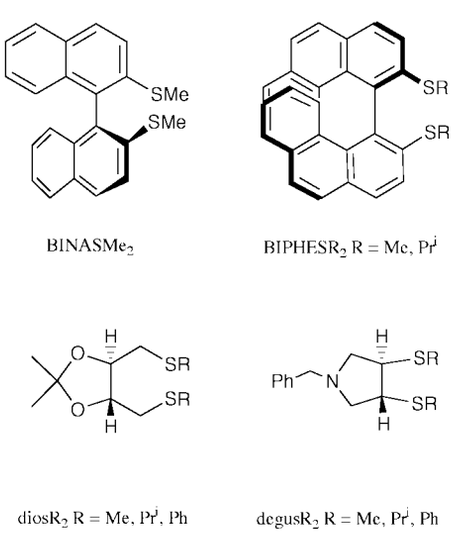
The asymmetric hydrogenation of prochiral compounds catalysed by chiral transition-metal complexes has been in widespread use in stereoselective organic synthesis[1] and some processes have found industrial applications.[2]

In the last few years excellent results using sugar derivative ligands in different types of asymmetric catalytic reactions have been obtained (Scheme 1).[3] Despite the accessibility and lower cost of carbohydrate synthons, their potential for providing chiral ligands has hardly been exploited. Moreover, sulfur ligands have been studied less than phosphorus ligands despite their advantages of lower cost, toxicity and oxidation.[4] To our knowledge, only Spescha[5] and recently our group[6] have reported the use of sugar-derivative ligands containing sulfur as a unique donor atom in asymmetric catalysis.



Scheme 1

Several reports involving the use of chiral dithioether ligands in asymmetric catalysis have demonstrated their potential utility.[7–11] Good conversions have been achieved in the hydroformylation of styrene with rhodium complexes containing the dithioethers BINASMe$_2$,[7] BIPHESR$_2$[8] and diosR$_2$[9] (R = Me or Pr^i), but low enantiomeric excesses have been obtained, which can be explained by the formation of an unfavorable mixture of diastereoisomers.[12] Better results have been obtained using iridium cationic complexes in the enantioselective hydrogenation of acrylic acids under mild conditions.[10,11] Only one diastereoisomer has been detected for olefinic complexes containing diosR$_2$[10] and degusR$_2$.[11] It should be noted that degusR$_2$ ligands with a rigid backbone and chiral center closer to the metal improved the enantioselectivity of the reaction much more than diosR$_2$ derivatives, which form a more flexible seven-membered chelate ring.

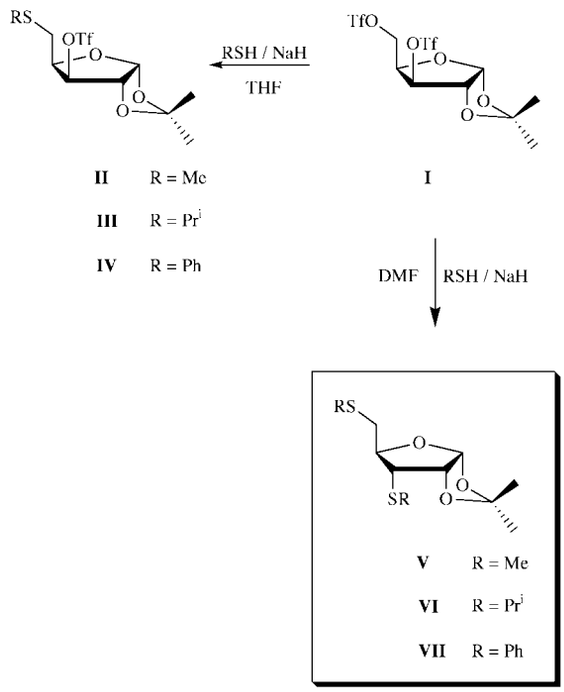


In this paper we report the synthesis of the first family of sugar-derivative dithioethers. The synthesis, characterisation and reactivity studies with H_2 of the related C_1 symmetrical iridium complexes with a six-membered dithioether chelate ring are discussed. The complexes have proven to be active in the asymmetric hydrogenation of prochiral acrylic acids at 1 bar of hydrogen and room temperature.

Results and discussion

Synthesis of the dithioethers

The reaction of 1,2-*O*-isopropylidene-3,5-di-*O*-trifluoromethanesulfonyl-D-xylofuranose **I**[6] with the sodium salt of methanethiol, propane-2-thiol or benzenethiol in tetrahydrofuran affords only the monosubstituted thioethers **II**–**IV** (Scheme 2). However, when the reaction is carried out under



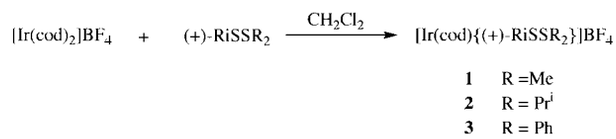
Scheme 2 Synthetic procedures for the preparation of ligands (+)-RiSSMe$_2$ **V**, (+)-RiSSPr$^i_2$ **VI** and (+)-RiSSPh$_2$ **VII**.

reflux for two days, dithioethers **V** and **VI** can be obtained in low yield (30 and 20%, respectively). When dimethylformamide is used as a solvent ligand **VII** is obtained and the yields of **V** and **VI** increase (51 and 37%, respectively). These yields are low because the nucleophilic attack (S_N2) on carbon C-3 takes place at the most sterically hindered face. This effect is more pronounced with ligand **VII** perhaps because of the greater rigidity of the phenyl groups. This unfavorable kinetics led to secondary reactions at higher temperatures, principally the elimination of the triflyl (CF_3SO_3) group.

Dithioethers **V** and **VI** were isolated as colorless liquids which are very stable at low temperature, **VII** as a white solid which is stable in air at room temperature. The dithioethers were characterised by elemental analysis, mass spectrometry and ^{1}H, ^{13}C NMR spectroscopy. Mass spectrometry shows the highest ions at *m*/*z* 250, 306 and 374, which correspond to the molecular weights of compounds **V**–**VII**, respectively. The obtained ^{1}H and ^{13}C NMR spectra are in agreement with those expected for these C_1 symmetrical ligands.

Synthesis of olefinic complexes

The reaction of the corresponding chiral dithioethers (+)-RiSSR$_2$ **V**–**VII** with [Ir(cod)$_2$]BF$_4$ in dichloromethane solution proceeded with the displacement of one cycloocta-1,5-diene ligand to produce the cationic complexes **1**–**3** (Scheme 3). The complexes were characterised by elemental analysis, FAB mass spectrometry, IR and ^{1}H, ^{13}C NMR spectroscopy. The FAB mass spectra show the highest ions at *m*/*z* 550, 607 and 674 which correspond to the loss of the BF$_4^-$ anion from the mononuclear species **1**, **2** and **3**, respectively. The IR spectra show a strong band between 1090 and 1050 cm^{-1} and a medium band



Scheme 3

at 450 cm^{-1} characteristic of the non-co-ordinated BF$_4^-$ anion in cationic complexes.[13] These complexes also have great air-stability even in solution.

Dithioether ligands create two stereogenic centers when they co-ordinate to a metal atom, so several stereoisomers (eight for complexes **1**–**3**) with different spatial arrangements of the SR substituents and different conformations of the six-membered chelate ring can be obtained.

The structure of the molecular cation [Ir(cod){(+)-RiSSR$_2$}]$^+$ could be revealed by ^{1}H and ^{13}C NMR spectroscopy (Table 1). The ^{1}H NMR spectra of iridium complexes **1** and **2** show the olefinic protons of the co-ordinated cyclooctadiene as broad signals. Two signals are observed for **3**. At −70 °C these signals are resolved into four, as expected for a C_1 symmetrical complex. For the *endo*- and *exo*-methylenic protons of cyclooctadiene only two broad signals were observed for complex **1** and three broad signals for **2** and **3**. This is probably due to an overlap of the broad signals. In the ^{13}C NMR spectra of **1**–**3** broad signals are observed for the olefinic and methylenic carbon atoms.

The signals from the dithioether ligands produced the expected NMR pattern for the ribofuranoside nucleus. The two MeS, Pr^{i}S and PhS groups appear in the ^{1}H and ^{13}C NMR as non-equivalent for complexes **1**, **2** and **3**, respectively. Thus, for **1** two signals for the MeS groups were observed in the ^{1}H and ^{13}C NMR spectra. For **2** the four diastereotopic methyl groups appear as four doublets at δ 1.47, 1.52, 1.57 and 1.63 ($^3J_{H\text{-}H}$ = 6.6 Hz) and the methinic protons appear as one broad signal, overlapped with those of protons H-5′, H-5 and H-3 of the furanoside ring. The ^{13}C NMR spectrum also show 4 signals for the methyl groups and two for the carbons of the methinic groups. The signals from the aromatic part of complex **3** are too close together and are not appropriately shaped to be determined reliably. The shape of the NMR spectra for all complexes is not affected when the sample is cooled to −70 °C and heated to 40 °C. In particular, the methyl, isopropyl and phenyl resonances do not show any splitting. These NMR results indicate that only one diastereomer is present for all complexes. Irradiation of the two methyl signals of the dithioether ligand in complex **1** only causes a significant NOE enhancement of the olefinic protons of the co-ordinated cyclooctadiene. This is consistent with an equatorial location for them.[12] For the two possible conformations (twist-boat and twist-chair) of the six-membered chelate ring with both methyl groups in equatorial position, molecular mechanics calculations (CERIUS 2) show that the twist-chair is the more stable conformer. For the related complexes with Pr^{i}S and PhS groups, NOE experiments and mechanics molecular calculations do not allow us to propose their stereochemistry.

In summary, NMR studies in combination with molecular mechanics show that the diastereomer present in solution for compound **1** has a twist-chair conformation with a (1*R*, 2*R*, 3*S*, 4*R*, S^1*S*, S^2*R*) dithioether configuration.

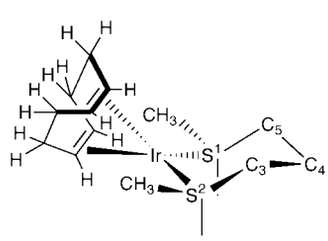
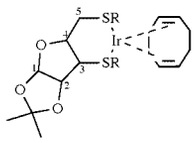


Table 1 The NMR spectroscopic data for complexes **1**–**3**[a]



	1		**2**		**3**	
Position	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1	5.85 (d) $^3J_{1\text{-}2}$ = 3.6	103.4	5.91 (d) $^3J_{1\text{-}2}$ = 3.6	105.8	5.74 (d) $^3J_{1\text{-}2}$ = 3.6	103.4
2	4.86 (dd) $^3J_{2\text{-}3}$ = 4.2	77.0	4.77 (dd) $^3J_{2\text{-}3}$ = 4.2	81.7	4.28 (dd) $^3J_{2\text{-}3}$ = 3.9	79.7
3	3.45 (m)	53.2	3.46 (br)	53.9	4.09 (m)	55.5
4	3.45 (m)	76.7	4.48 (ddd) J = 10.8, J = 10.5 J = 2.1	81.2	4.09 (m) $^3J_{5\text{-}4}$ = 2.4	74.9
5	2.99 (m)	38.5	3.46 (br)	42.8	3.56 (dd) $^2J_{5'\text{-}5}$ = 12.9	41.4
5′	2.99 (m)		3.46 (br)		3.45 (dd) $^3J_{5'\text{-}4}$ = 10.2	
*C*Me		113.3		113.7		111.9
C*Me*	1.34 (s)	26.1	1.34 (s)	26.5	1.16 (s)	26.6
C*Me*	1.57 (s)	26.3	1.57 (s)	26.7	1.40 (s)	26.6
SME	2.53 (s)	16.3				
	2.62 (s)	20.7				
Me			1.47 (d), 1.52 (d) 1.57 (d), 1.63 (d) $^3J_{\text{H-H}}$ = 6.6	22.8, 23.3 23.9, 24.3		
SCH			3.46 (br)	37.5, 39.1		
Ph					7.4–7.8 (m)	130–134
CH_2	1.85 (br, 4 H)	31.0 (br)	1.80 (br, 2 H)	30.8 (br)	1.69 (br, 4 H)	28.5 (br)
	2.10 (br, 4 H)	31.5 (br)	1.98 (br, 2 H)	32.8 (br)	1.89 (br, 2 H)	30.7 (br)
			2.25 (br, 4 H)	34.9 (br)	2.13 (br, 2 H)	
CH=	4.25 (br, 4 H)	74.4 (br) 79.0 (br)	4.6 (br, 4 H)	79.2 (br)	3.73 (m, 2 H) 4.22 (m, 2 H)	79.4 (br) 80.0 (br)

[a] Chemical shifts in ppm; coupling constants in Hz; room temperature; ^{1}H and ^{13}C NMR in CD_2Cl_2. Abbreviations: s, singlet; d, doublet; dd, double doublet; ddd, double double doublet; m, multiplet; br, broad.

Reactivity of the olefinic complexes with H_2

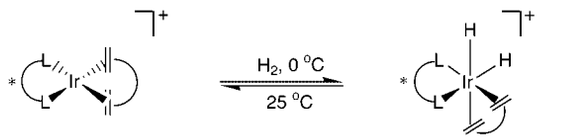
Transition-metal hydride complexes have been the focus of considerable research because of their prominent role in many catalytic hydrogenation processes.[14] The oxidative addition of hydrogen is the rate-determining step for the asymmetric hydrogenation of acrylic acid derivatives using rhodium complexes which contain chiral diphosphines[15] and diphosphites.[16] For this reason we believe that is interesting to study the reactivity of the olefinic dithioether complexes synthesized with H_2.

Bubbling H_2 at 0 °C through CD_2Cl_2 solutions of [Ir(cod)-{(+)-RiSSR$_2$}]BF_4 **1**–**3** complexes gave the corresponding *cis*-dihydridoolefin species **4**–**6** in quantitative yield. In these species both the metal and the sulfur are stereogenic centers, so the number of possible diastereoisomers in solution increases. In the high-field region of the ^{1}H NMR spectra of the CD_2Cl_2 solutions of **4** and **6** six signals of different intensities can be observed (ratio 70:15:15) at δ −12.9, −13.5, −12.7, −13.3, −13.3 and −14.3 for **4** and at δ −13.1, −13.4, −12.6, −13.2, −13.5 and −13.7 for **6**. These signals may be from three diastereomeric *cis*-dihydridoiridium complexes. In a CD_2Cl_2 solution of complex **5** four signals with the same intensity are observed at δ −13.2, −14.2 and −13.3, −14.7, which may mean that there are two diastereomeric *cis*-dihydridoiridium complexes.

In the low-field region of the ^{1}H NMR spectrum of complex **4**, the signals from the major isomer can be attributed. Thus, the two MeS groups appear as two singlets at δ 2.68 and 3.12 (shifted to a lower field than for olefinic complex **1**). In the furanoside part of the dithioether ligand the anomeric (H-1) and the two methyl protons are well defined at δ 5.84 as a doublet ($^3J_{\text{H1-H2}}$ = 3.6 Hz) and as two singlets at δ 1.29 and 1.47, respectively. For the other protons, however, broad signals have been observed (H2: δ 4.89. H3: δ 4.05. H4: δ 3.72. H5. δ 3.41. H5′ δ 3.21). The olefinic protons of the co-ordinated cyclooctadiene appear as two multiplets at δ 4.22 and 4.79. For the *endo*- and *exo*-methylenic protons of the cyclooctadiene three multiplets were observed. The ^{1}H NMR also shows small signals from the minor isomers. Clearly distinguishable and worth mentioning are the doublets at δ 5.74 ($^3J_{\text{H1-H2}}$ = 3.3) and 5.80 ($^3J_{\text{H1-H2}}$ = 3.6 Hz) for the anomeric protons. For complexes **5** and **6** there are signals which correspond to cyclooctadiene and dithioether ligands. For **5** the anomeric protons of the two isomers appear as two doublets (ratio 50:50) at δ 5.82 ($^3J_{\text{H1-H2}}$ = 2.7) and 5.88 ($^3J_{\text{H1-H2}}$ = 3.0 Hz) respectively.

The relative abundance of the dihydrido diastereomers in solution does not change with temperature and shows no interconversion from −70 to 10 °C. When the temperature increases to 25 °C hydrogen is lost and the parent complexes are recovered. This indicates that the equilibrium of the *cis*-dihydridoiridium complexes in solution with the parent complexes depends on the temperature. This behaviour has also been observed for related complexes[10,11] (Scheme 4).

All attempts to isolate these *cis*-dihydridoiridium complexes produced the corresponding olefinic iridium(I) complexes even at −70 °C under a hydrogen atmosphere. The nature of the hydrido ligands was confirmed by measuring $T_{1\text{min}}$ using ^{1}H relaxation rates.[17] For all complexes the hydride resonances have $T_{1\text{min}}$ values around 250 ms in CD_2Cl_2 at −75 °C and 300 MHz. These values are consistent with classical hydride.[17]

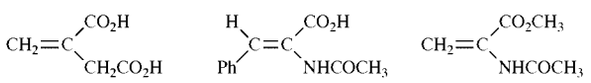


4 L–L = (+) -RiSSMe$_2$
5 L–L = (+) -RiSSPr$^i_2$
6 L–L = (+) -RiSSPh$_2$

Scheme 4

Hydrogenation

The use of cationic complexes with chiral dithioether ligands is an attractive approach for the catalytic hydrogenation of prochiral olefins, since good conversions and enantioselectivities are obtained without the addition of phosphorus ligands under very mild conditions.[10,11] Dithioether ligands **V**–**VII** have been used in the iridium asymmetric hydrogenation of itaconic acid **VIII**, (*Z*)-α-(acetamido)cinnamic acid **IX** and methy α-(acetamido)acrylate **X** at room temperature under



VIII **IX** **X**

atmospheric pressure of H_2. The catalytic system was generated *in situ* from $[Ir(cod)_2]BF_4$ and the corresponding dithioether ligand in dichloromethane. Conversion and enantioselectivity results are shown in Table 2.

The change of the substituent of the dithioethers produces an important effect on the rate and optical induction. Thus, the conversions and optical inductions are higher for the precursor containing the bulky and electron-rich ligand **VI**. The hydrogenation of **VIII** proceeded with higher rates and higher optical inductions than that of **IX** and especially **X** for all catalytic systems. These results show that the presence of carboxylic groups in the substrates enhances the reaction rate and enantioselectivity of the process. Thus, with the precursor containing the ligand (+)-RiSSPr$^i_2$ complete hydrogenation of itaconic acid is achieved after 12 h with an enantiomeric excess (e.e.) of 62%, while only 45 and 19% conversion and 37 and 13% e.e. are obtained in the hydrogenation of **IX** and **X**, respectively. This behaviour contrasts with phosphine systems where much better e.e.s were usually observed for substrates with an amido group such as **IX** and **X** than for itaconic acid.[18]

These results, using a C_1 dithioether with a six-membered chelate ring, are in the same order as the best e.e. values reported for the same substrates when a C_2 symmetrical dithioether degusR$_2$ with a more rigid five-membered chelate ring was used and much better than for C_2 symmetrical dithioethers diosR$_2$ with a seven-membered chelate ring.

Table 2 Hydrogenation results[a] with $[Ir(cod)]^+$/dithioether

Dithioether	Substrate	*t*/h	Conversion (%)	e.e.(%)
(+)-RiSSMe$_2$	**VIII**	12	35	14 (*R*)
	IX	12	8	nd[b]
	X	16	6	4 (*R*)
(+)-RiSSPr$^i_2$	**VIII**	12	100	62 (*R*)
	IX	12	45	37 (*S*)
	X	12	19	13 (*R*)
(+)-RiSSPh$_2$	**VIII**	12	100	17 (*R*)
	IX	12	45	12 (*S*)
	X	12	11	7 (*R*)

[a] At 20 °C and 1 atm of H_2. Solvent 6 ml, CH_2Cl_2. Substrate : precursor = 100 : 1. [b] Not determined.

Experimental

General comments

All syntheses were performed by standard Schlenk techniques under a nitrogen atmosphere. The complex $[Ir(cod)_2]BF_4$[13] and the compound 1,2-*O*-isopropylidene-3,5-bis(trifluoromethanesulfanyl)-α-D-xylofuranose[6] were prepared by previously described methods. Solvents were purified by standard procedures. All other reagents were used as commercially available.

Elemental analyses were performed on a Carlo Erba EA-1108 instrument. The ^1H and ^{13}C-{^1H} NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer. Chemical shifts are relative to $SiMe_4$ (^1H and ^{13}C) as internal standard. All assignments in NMR spectra were determined by means of COSY and heteronuclear correlation (HETCOR) spectra. Standard pulse sequences were employed for ^1H 2-D NOESY.[19] The phase-sensitive NOESY experiments used mixing times of 0.4 s. Proton T_1 studies were performed using the standard inversion recovery 180°–τ–90° pulse sequence method.[17a] Infrared spectra were recorded on a Midac Grams/386 spectrophotometer, EI mass spectra on an HP 5989 A spectrometer. A VG-Autospect was used for FAB mass spectral analyses. The matrix was *m*-nitrobenzyl alcohol. Optical rotations were measured at 25 °C on a Perkin-Elmer 241 MC polarimeter. The specific rotations are given in deg cm^3 g^{-1} dm^{-1} units; the concentration is given in 10^{-2} g cm^{-3} units. The reaction under 1 atm of H_2 was performed in a previously described hydrogen vacuum line.[20]

Computational details

The molecular mechanics calculations were carried out with the program CERIUS 2[21] and the force field UFF developed by Rappe and co-workers.[22] Electrostatic interactions were taken into account from atomic charges generated by the Qeq method.[23]

Ligand synthesis

1,2-*O*-Isopropylidene-5-methylsulfanyl-3-*O*-trifluoromethanesulfonyl-α-D-(−)-xylofuranose II. A suspension of NaH (0.56 g, 23 mmol) in paraffin, cleaned twice in hexane, in THF (15 ml) was cooled to −78 °C and methanethiol (0.5 ml, 9 mmol) at −78 °C was added. The resulting solution was stirred and the temperature raised to 0 °C. After 5 min the solution was cooled at −78 °C and a solution of compound **I** (1 g, 2.2 mmol) in THF (10 ml) added. After 1 h at room temperature water (50 ml) was added and the solvent evaporated and extracted with dichloromethane (3 × 50 ml). The extract was dried over magnesium sulfate and concentrated. The residue was purified by column chromatography (hexane–ethyl acetate, 10 : 1) to give a white solid (620 mg, 80%) (Found: C, 34.36; H, 4.56; S, 17.89. Calc. for $C_{10}H_{15}F_3O_6S_2$: C, 34.09; H, 4.29; S, 18.20%). δ_H(300 MHz, $CDCl_3$, $SiMe_4$) 1.31 (s, 3 H, CMe), 1.49 (s, 3 H, CMe), 2.17 (s, 3 H, SMe), 2.71 (dd, 1 H, H-5′, $^2J_{5'\text{-}5}$ = 13.8, $^3J_{5'\text{-}4}$ = 7.2), 2.79 (dd, H-5, $^2J_{5\text{-}5'}$ = 13.8, $^3J_{5\text{-}4}$ = 6.9), 4.44 (ddd, 1 H, H-4, $^3J_{4\text{-}5'}$ = 7.2, $^3J_{4\text{-}3}$ = 3.0, $^3J_{4\text{-}5}$ = 6.9), 4.73 (d, 1 H, H-2, $^3J_{2\text{-}1}$ = 3.6), 5.21 (d, 1 H, H-3, $^3J_{3\text{-}4}$ = 3.0 Hz) and 5.98 (d, 1 H, H-1, $^3J_{1\text{-}2}$ = 3.6 Hz). δ_C(75 MHz, $CDCl_3$) 16.2 (SMe), 26.0 (C*Me*), 26.3 (C*Me*), 30.9 (C-5), 78.5 (C-4), 82.8 (C-2), 88.4 (C-3), 104.4 (C-1), 112.8 (*C*Me) and 118.3 (q, CF_3, $^1J_{C\text{-}F}$ = 319 Hz). $[\alpha]_D^{20}$ = −47.9 (*c* = 1 in $CHCl_3$).

1,2-*O*-Isopropylidene-5-isopropylsulfanyl-3-*O*-trifluoromethanesulfonyl-α-D-(−)-xylofuranose III. A solution of 2-propanethiol (0.52 ml, 5.6 mmol) in THF (6 ml) was added to a suspension of NaH (0.56 g, 23 mmol) in paraffin, cleaned twice in hexane, in THF (8 ml). After 30 min at room temperature the suspension was cooled at 0 °C and a solution of compound **I** (1 g, 2.2 mmol) in THF (10 ml) added. After 1 h at room temperature water (50 ml) was added and the solvent evaporated and

extracted with dichloromethane (3 × 50 ml). The extract was dried over magnesium sulfate and concentrated. The residue was purified by column chromatography (hexane–ethyl acetate, 10:1) to give a colourless liquid (315 mg, 38%) (Found: C, 38.03; H, 4.99; S, 17.05. Calc. for $C_{12}H_{19}F_3O_6S_2$: C, 37.89; H, 5.03; S, 16.86%). δ_H(300 MHz, $CDCl_3$, $SiMe_4$) 1.25 (d, 3 H, Me, $^3J_{H\text{-}H}$ = 4.2), 1.28 (d, 3 H, Me, $^3J_{H\text{-}H}$ = 3.9), 1.32 (s, 3 H, CMe), 1.50 (s, 3 H, CMe), 2.71 (dd, 1 H, H-5′, $^2J_{5'\text{-}5}$ = 13.5, $^3J_{5'\text{-}4}$ = 7.5), 2.91 (dd, H-5, $^2J_{5\text{-}5'}$ = 13.5, $^3J_{5\text{-}4}$ = 7.8), 3.00 (s, 1 H, SCH), 4.41 (ddd, 1 H, H-4, $^3J_{4\text{-}5'}$ = 7.5, $^3J_{4\text{-}3}$ = 2.4, $^3J_{4\text{-}5}$ = 7.8), 4.73 (d, 1 H, H-2, $^3J_{2\text{-}1}$ = 3.6), 5.21 (d, 1 H, H-3, $^3J_{3\text{-}4}$ = 2.4) and 5.98 (d, 1 H, H-1, $^3J_{1\text{-}2}$ = 3.6 Hz). δ_C(75 MHz, $CDCl_3$) 23.2 (Me), 23.3 (Me), 26.2 (C*Me*), 26.4 (C*Me*), 27.5 (C-5), 35.8 (SCH), 78.8 (C-4), 82.8 (C-2), 88.3 (C-3), 104.4 (C-1), 112.8 (*C*Me) and 118.3 (q, CF_3, $^1J_{C\text{-}F}$ = 318 Hz). $[\alpha]_D^{20}$ = −59.4 (*c* = 1 in $CHCl_3$).

1,2-*O*-Isopropylidene-5-phenylsulfanyl-3-*O*-trifluoromethanesulfonyl-α-D-(−)-xylofuranose IV. A solution of benzenethiol (0.5 ml, 4.9 mmol) in THF (6 ml) was added to a suspension of NaH (0.56 g, 23 mmol) in paraffin, cleaned twice in hexane, in THF (8 ml). After 30 min at room temperature the suspension was cooled at 0 °C and a solution of compound **I** (1 g, 2.2 mmol) in THF (10 ml) added. After 1 h at room temperature water (50 ml) was added and the solvent evaporated and extracted with dichloromethane (3 × 50 ml). The extract was dried over magnesium sulfate and concentrated. The residue was purified by column chromatography (hexane–ethyl acetate, 10:1) to give a white solid (537 mg, 59%) (Found: C, 43.86; H, 4.06; S, 15.91. Calc. for $C_{15}H_{17}F_3O_6S_2$: C, 43.47; H, 4.13; S, 15.47%). δ_H(300 MHz, $CDCl_3$, $SiMe_4$) 1.31 (s, 3 H, CMe), 1.38 (s, 3 H, CMe), 3.00 (dd, 1 H, H-5′, $^2J_{5'\text{-}5}$ = 13.8, $^3J_{5'\text{-}4}$ = 7.8), 3.29 (dd, H-5, $^2J_{5\text{-}5'}$ = 13.8, $^3J_{5\text{-}4}$ = 6.6), 4.36 (ddd, 1 H, H-4, $^3J_{4\text{-}5'}$ = 7.8, $^3J_{4\text{-}3}$ = 2.4, $^3J_{4\text{-}5}$ = 6.6), 4.75 (d, 1 H, H-2, $^3J_{2\text{-}1}$ = 3.9), 5.25 (d, 1 H, H-3, $^3J_{3\text{-}4}$ = 2.4), 5.99 (d, 1 H, H-1, $^3J_{1\text{-}2}$ = 3.9) and 7.2–7.5 (m, 5 H, CH=, Ph). δ_C(75 MHz, $CDCl_3$) 26.3 (C*Me*), 31.3 (C-5), 77.2 (C-4), 82.9 (C-2), 87.9 (C-3), 104.4 (C-1), 113.0 (*C*Me), 118.3 (q, CF_3, $^1J_{C\text{-}F}$ = 319), 127.4, 129.3, 131.0 (CH=, Ph) and 133.9 (C, Ph). $[\alpha]_D^{20}$ = −81.7 (*c* = 1 in $CHCl_3$).

1,2-*O*-Isopropylidene-3,5-bis(methylsulfanyl)-α-D-(+)-ribofuranose V. A suspension of NaH (0.56 g, 23 mmol) in paraffin, cleaned twice in hexane, in DMF (15 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 raised to 0 °C. After 5 min the solution was cooled at −78 °C and a solution of compound **I** (1 g, 2.2 mmol) in DMF (10 ml) added. After 36 h at 90 °C water (150 ml) was added and extracted with dichloromethane (5 × 50 ml) and washed with water. The extract was dried over magnesium sulfate and concentrated. The residue containing **II** and **V** was purified by column chromatography (hexane–ethyl acetate, 10:1) to give a colourless liquid (272 mg, 51%) (Found: C, 47.75; H, 7.57; S, 24.99. Calc. for $C_{10}H_{18}O_3S_2$: C, 47.97; H, 7.25; S, 25.61%). *m*/*z* = 250 (M^+). δ_H(300 MHz, $CDCl_3$, $SiMe_4$) 1.31 (s, 3 H, CMe), 1.49 (s, 3 H, CMe), 2.18 (s, 3 H, SMe), 2.22 (s, 3 H, SMe), 2.72 (dd, 1 H, H-5′, $^2J_{5'\text{-}5}$ = 14.4 Hz, $^3J_{5'\text{-}4}$ = 5.1), 2.94 (dd, H-3, $^3J_{3\text{-}4}$ = 10.2, $^3J_{3\text{-}2}$ = 4.2), 3.01 (dd, 1 H, H-5, $^2J_{5\text{-}5'}$ = 14.4, $^3J_{5\text{-}4}$ = 3.0), 4.18 (ddd, 1 H, H-4, $^3J_{4\text{-}5'}$ = 5.1, $^3J_{4\text{-}3}$ = 10.2, $^3J_{4\text{-}5}$ = 3.0), 4.73 (dd, H-2, $^3J_{2\text{-}1}$ = 3.9, $^3J_{2\text{-}3}$ = 4.2) and 5.78 (d, 1 H, H-1, $^3J_{1\text{-}2}$ = 3.9 Hz). δ_C(75 MHz, $CDCl_3$) 15.3 (SMe), 17.2 (SMe), 26.2 (C*Me*), 26.4 (C*Me*), 35.3 (C-5), 51.4 (C-3), 80.6 (C-4), 81.2 (C-2), 104.1 (C-1) and 112.1 (*C*Me). $[\alpha]_D^{20}$ = +78.7 (*c* = 1 in $CHCl_3$).

1,2-*O*-Isopropylidene-3,5-bis(isopropylsulfanyl)-α-D-(+)-ribofuranose VI. A solution of 2-propanethiol (0.52 ml, 5.6 mmol) in DMF (6 ml) was added to a suspension of NaH (0.56 g, 23 mmol) in paraffin, cleaned twice in hexane, in DMF (8 ml). After 30 min at room temperature the suspension was cooled at 0 °C and a solution of compound **I** (1 g, 2.2 mmol) in DMF (10 ml) added. After 36 h at 90 °C water (150 ml) was added and extracted with dichloromethane (5 × 50 ml) and washed with water. The extract was dried over magnesium sulfate and concentrated. The residue containing **III** and **VI** was purified by column chromatography (hexane–ethyl acetate, 10:1) to give colourless liquid (238 mg, 37%) (Found: C, 54.21; H, 8.45; S, 19.87. Calc. for $C_{14}H_{26}O_3S_2$: C, 54.87; H, 8.55; S, 20.92%). *m*/*z* = 306 (M^+). δ_H(300 MHz, $CDCl_3$, $SiMe_4$) 1.25 (m, 12 H, Me), 1.35 (s, 3 H, CMe), 1.52 (s, 3 H, CMe), 2.79 (dd, 1 H, H-5′, $^2J_{5'\text{-}5}$ = 14.1, $^3J_{5'\text{-}4}$ = 4.5), 3.08 (m, 4 H, H-5, H-3, SCH), 4.13 (m, H-4), 4.67 (dd, H-2, $^3J_{1\text{-}2}$ = 3.6, $^3J_{2\text{-}3}$ = 4.2) and 5.80 (d, 1 H, H-1, $^3J_{1\text{-}2}$ = 3.6 Hz). δ_C(75 MHz, $CDCl_3$) 23.2 (Me), 23.3 (Me), 23.5 (Me), 24.3 (Me), 26.2 (C*Me*), 26.5 (C*Me*), 31.1 (C-5), 35.7 (SCH), 36.0 (SCH), 48.8 (C-3), 80.7 (C-4), 81.8 (C-2), 104.2 (C-1) and 111.9 (*C*Me). $[\alpha]_D^{20}$ = +56.4 (*c* = 1 in $CHCl_3$).

1,2-*O*-Isopropylidene-3,5-bis(phenylsulfanyl)-α-D-(+)-ribofuranose VII. A solution of benzenethiol (0.5 ml, 4.9 mmol) in DMF (6 ml) was added to a suspension of NaH (0.56 g, 23 mmol) in paraffin, cleaned twice in hexane, in DMF (8 ml). After 30 min at room temperature the suspension was cooled at 0 °C and a solution of compound **I** (1 g, 2.2 mmol) in DMF (10 ml) added. After 48 h at 90 °C water (150 ml) was added, the solvent was evaporated and the residue extracted with dichloromethane (5 × 50 ml) and washed with water. The extract was dried over magnesium sulfate and concentrated. The residue was purified by column chromatography (hexane–ethyl acetate, 2:1) as a white solid (123 mg, 15%), mp 129–130 °C (Found: C, 63.84; H, 5.99; S, 16.99. Calc. for $C_{20}H_{22}O_3S_2$: C, 64.14; H, 5.92; S, 17.12%). *m*/*z* = 374 (M^+). δ_H(300 MHz, $CDCl_3$, $SiMe_4$) 1.36 (m, 3 H, CMe), 1.54 (s, 3 H, CMe), 3.04 (dd, 1 H, H-5′, $^2J_{5'\text{-}5}$ = 14.4, $^3J_{5'\text{-}4}$ = 4.8), 3.40 (m, 2 H, H-5, H-3), 4.25 (m, H-4), 4.75 (dd, H-2, $^3J_{2\text{-}1}$ = 3.3, $^3J_{2\text{-}3}$ = 3.6), 5.76 (d, 1 H, H-1, $^3J_{1\text{-}2}$ = 3.3 Hz) and 7.1–7.5 (m, 10 H, CH=, Ph). δ_C(75 MHz, $CDCl_3$) 26.4 (C*Me*), 26.6 (C*Me*), 35.7 (C-5), 53.4 (C-3), 80.18 (C-4), 81.3 (C-2), 104.3 (C-1), 112.5 (*C*Me), 126.2, 126.6, 128.9, 129.3, 129.7 and 131.8 (CH=, Ph). $[\alpha]_D^{20}$ = +62.4 (*c* = 1 in $CHCl_3$).

Preparation of iridium complexes

[Ir(cod){(+)-RiSSMe$_2$}]BF$_4$ 1. The compound was prepared by adding an excess of ligand (27 mg, 0.11 mmol) to a dichloromethane solution of $[Ir(cod)_2]BF_4$ (49.7 mg, 0.1 mmol), which produced an immediate change from brown-red to orange. After 5 min the solvent was evaporated and the orange solid cleaned twice with cold hexane and vacuum dried (54 mg, 85%) (Found: C, 34.25; H, 4.61; S, 10.12. Calc. for $C_{18}H_{30}BF_4IrO_3S_2$: C, 33.85; H, 4.74; S, 10.05%). *m*/*z*: 550 (M^+).

[Ir(cod){(+)-RiSSPr$^i_2$}]BF$_4$ 2. The compound was prepared as above by adding an excess of ligand (34 mg, 0.11 mmol) to a dichloromethane solution of $[Ir(cod)_2]BF_4$ (49.7 mg, 0.1 mmol), 58 mg (84%) (Found: C, 37.86; H, 5.59; S, 9.78. Calc. for $C_{22}H_{38}BF_4IrO_3S_2$: C, 38.03; H, 5.52; S, 9.23%). *m*/*z* 607 (M^+).

[Ir(cod){(+)-RiSSPh$_2$}]BF$_4$ 3. The compound was prepared as above by adding an excess of ligand (41 mg, 0.11 mmol) to a dichloromethane solution of $[Ir(cod)_2]BF_4$ (49.7 mg, 0.1 mmol), 63 mg (82%) (Found: C, 43.69; H, 4.61; S, 9.18. Calc. for $C_{28}H_{34}BF_4IrO_3S_2BF_4Ir$: C, 44.09; H, 4.50; S, 8.41%) *m*/*z* 674 (M^+).

***In situ* hydrido complexes.** In a typical experiment hydrogen was bubbled through a solution of $[Ir(cod)_2]BF_4$ (24.7 mg, 0.05 mmol) and ligand (0.05 mmol) in CD_2Cl_2 (0.5 ml) at 0 °C for 15 min. The solution was then transferred to an NMR spectrometer tube and the ^1H NMR were recorded at the desired temperature (see text for ^1H NMR data and characterisation).

Hydrogenation of prochiral olefins

In a typical run a Schlenk was filled with a dichloromethane (6 ml) solution of substrate (1 mmol) and catalyst precursor (0.01 mmol). It was then purged three times with H_2 and vacuum. The reaction mixture was then shaken under H_2 (1 atm) at 293 K. After a desired reaction time, the solvent was removed. The following procedures were used to isolate the hydrogenation product. For methylsuccinic acid and *N*-acetylphenylalanine, the residue was dissolved in 0.5 M NaOH and separated from the insoluble catalyst by filtration. The filtrate was acidified with diluted HCl, extracted with diethyl ether, and washed with a little water. The ether phase was dried over sodium sulfate and evaporated to dryness. For *N*-acetylalanine methyl ester, gas chromatography analyses were performed in a Hewlett-Packard 5890A instrument (fused silica capillary column, 25 m × 0.25 mm, permabond L-Chirasil-Val).

Acknowledgements

We thank the Spanish Ministerio de Educación y Cultura and the Generalitat de Catalunya (CIRIT) for financial support (PB97-0407-CO5-01) and the Generalitat de Catalunya (CIRIT) for awarding a research grant (to O. P.). We are also very much indebted to Professor Sergio Castillón for his very useful discussions and suggestions.

References

1 H. Takaya, T. Onta and R. Noyori, in *Catalytic Asymmetric Synthesis*, ed. I. Ojima, VCH, New York, 1993, ch. 1; R. Noyori, in *Asymmetric Catalysis in Organic Synthesis*, Wiley, New York, 1994, ch. 2, p. 16; J. M. Brown, *Chem. Soc. Rev.*, 1993, 25; H. Brunner, *Top. Stereochem.*, 1988, **18**, 129; J. M. Brown, in *Insights into Speciality Inorganic Chemicals*, ed. D. Thompson, The Royal Society of Chemistry, Cambridge, 1995, ch. 6.

2 S. Akutagawa, in *Asymmetric Hydrogenation with Ru-BINAP: Chirality in Industry*, eds. A. N. Collins, G. N. Sheldrake and J. Crosby, Wiley, Chichester, 1992, p. 235; S. Kotha, *Tetrahedron*, 1994, **50**, 3639; S. Akutagawa, in *Asymmetric Hydrogenation with Ru-BINAP: Catalysis of Organic Reactions*, eds. M. Scaros and M. L. Prunier, Marcel Dekker, New York, 1994, p. 135; *Appl. Catal. A, Gen.*, 1995, **128**, 171.

3 (*a*) G. J. H. Buisman, M. E. Martin, E. J. Voss, A. Klootwijk, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Tetrahedron Asymmetry*, 1995, **6**, 719; (*b*) M. Beller, J. G. E. Krauter and A. Zapf, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 772; (*c*) M. T. Reetz and S. R. Waldvogel, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 865; (*d*) DuPont, A. L. Casalnuovo and T. V. RajanBabu, *U.S. Pat.*, 5 484 902, 16 January, 1966; (*e*) T. V. RajanBabu and A. L. Casalnuovo, *Pure Appl. Chem.*, 1994, **66**, 1535; (*f*) D. Lafont, D. Sinou and G. Descotes, *J. Organomet. Chem.*, 1979, **169**, 87; (*g*) R. Selke, *J. Organomet. Chem.*, 1989, **370**, 249; (*h*) A. Iida and M. Yamashita, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2365; (*i*) T. V. RajanBabu and T. A. Ayers, *Tetrahedron Lett.*, 1994, **35**, 4295; (*j*) O. Pàmies, G. Net, A. Ruiz and C. Claver, unpublished results; (*k*) T. V. RajanBabu, T. Ayers, G. A. Halliday, K. K. You, J. C. Calabrese and A. L. Casalnuovo, *J. Org. Chem.*, 1997, **62**, 6012.

4 F. Fache, P. Gamez, F. Nour and M. Lemaire, *J. Mol. Catal.*, 1993, **85**, 131.

5 M. Spescha, *Helv. Chim. Acta*, 1993, **76**, 1833.

6 O. Pàmies, G. Net, A. Ruiz, C. Bo, J. M. Poblet and C. Claver, *J. Organomet. Chem.*, 1999, **586**, 125.

7 C. Claver, S. Castillón, N. Ruiz, G. Deloghu, D. Fabbri and S. Gladiali, *J. Chem. Soc., Chem. Commun.*, 1993, 1833.

8 N. Ruiz, A. Aaliti, F. Forniés, A. Ruiz, C. Claver, C. J. Cardin, D. Fabbri and S. Gladiali, *J. Organomet. Chem.*, 1997, **79**, 545.

9 A. Orejón, A. M. Masdeu-Bultó, R. Echarri, M. Dieguéz, J. Forniés-Camer, C. Claver and C. J. Cardin, *J. Organomet. Chem.*, 1998, **559**, 23.

10 M. Diéguez, A. Orejón, A. M. Masdeu-Bultó, R. Echarri, S. Castillón, C. Claver and A. Ruiz, *J. Chem. Soc., Dalton Trans.*, 1997, 4611.

11 M. Diéguez, A. Ruiz, C. Claver, M. M. Pereira and A. M. d'A. R. Gonsalves, *J. Chem. Soc., Dalton Trans.*, 1998, 3517.

12 S. Gladiali, D. Fabbri, L. Kollàr, C. Claver, N. Ruiz, A. Alvarez-Larena and J. F. Piniella, *Eur. J. Inorg. Chem.*, 1998, 113.

13 M. Green, T. A. Kuc and S. H. Taylor, *J. Chem. Soc. A*, 1971, 2334; K. Nakamoto, in *Infrared and Raman Spectra of Inorganic and Co-ordination Compounds*, Wiley, New York, 1978.

14 B. R. James, in *Homogeneous Hydrogenation*, Wiley, New York, 1973; P. A. Chaloner, M. A. Esteruelas, F. Joó and L. A. Oro, in *Homogeneous Hydrogenation*, Kluwer, Dordrecht, 1994, ch. 4.

15 C. R. Landis and J. Halpern, *J. Am. Chem. Soc.*, 1987, **109**, 1746.

16 O. Pàmies, G. Net, A. Ruiz and C. Claver, unpublished results.

17 (*a*) D. G. Hamilton and R. H. Crabtree, *J. Am. Chem. Soc.*, 1998, **110**, 4126; (*b*) J. C. Lee, jun., W. Yao and R. H. Crabtree, *Inorg. Chem.*, 1996, **35**, 695.

18 A. Togni, C. Breutel, A. Schayder, F. Spindler, H. Landert and A. Tijani, *J. Am. Chem. Soc.*, 1994, **116**, 4062.

19 D. J. States, R. A. Haberkorn and D. J. Ruben, *J. Magn. Reson.*, 1982, **48**, 286.

20 C. Cativiela, J. Fernandez, J. A. Mayoral, E. Melendez, R. Usón, L. A. Oro and M. J. Fernandez, *J. Mol. Catal.*, 1992, **16**, 19.

21 CERIUS 2, version 3.5, Molecular Simulations Inc., San Diego, USA, 1997.

22 L. A. Castonguay and A. K. Rappe, *J. Am. Chem. Soc.*, 1992, **114**, 583; A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard-III and W. M. Skiff, *J. Am. Chem. Soc.*, 1992, **114**, 10024; A. K. Rappe and K. S. Colwell, *Inorg. Chem.*, 1993, **32**, 3438.

23 A. K. Rappe, C. J. Casewit, and W. A. Goddard-III, *J. Phys. Chem.*, 1991, **95**, 3358.

Paper 9/05396D