

Synthesis and stereochemical study of new complexes of Pd and Pt with chiral dithioether ligands

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New palladium(II) and platinum(II) complexes with two families of chiral dithioether ligands, (–)-1-benzyl-3,4-bis(methylsulfanyl)pyrrolidine (–)-degusMe₂, (–)-1-benzyl-3,4-bis(isopropylsulfanyl)pyrrolidine (–)-degusPrⁱ₂, (+)-1-benzyl-3,4-bis(phenylsulfanyl)pyrrolidine (+)-degusPh₂, (–)-2,2-dimethyl-4,5-bis(methylsulfanylmethyl)-1,3-dioxolane (–)-diosMe₂ and (–)-4,5-bis(isopropylsulfanylmethyl)-2,2-dimethyl-1,3-dioxolane (–)-diosPrⁱ₂, have been prepared and characterised by NMR. The complexes [PdCl₂{(–)-degusMe₂}], [PdCl₂{(+)-degusPh₂}] and [PdCl₂{(–)-diosMe₂}] show a mixture of two diastereomers in solution at room temperature. VT-NMR indicates that there is no interconversion between diastereomers at room temperature. Complex [Pt(cod){(–)-diosMe₂}][BF₄]₂ is extremely fluxional and its diastereomers did not show isolated NMR resonances even at –90 °C. The complexes [PdCl₂{(–)-degusPrⁱ₂}], [PdCl₂{(–)-diosPrⁱ₂}] and [Pt(cod){(–)-diosPrⁱ₂}][BF₄]₂, which contain a more hindered ligand, seem to be well suited for use in enantioselective catalysis because only one diastereomer is present.

Introduction

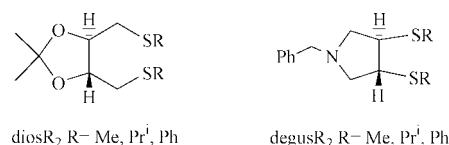
Catalytic asymmetric synthesis using organometallic complexes has become one of the most active areas of research in modern organic synthesis.¹ In this area the search for and development of new chiral complexes, and a better understanding of their properties, play a fundamental role in revealing the mechanisms of catalytic processes.^{1,2}

The most commonly studied and employed organometallic complexes contain phosphorus ligands. This is mainly due to the excellent results obtained with phosphines in different catalytic reactions.¹ However, interest in sulfur ligands has increased over the last few years because of the promising results obtained by using thioether and dithioether ligands in different reactions.³ Palladium complexes containing a thioether group have produced excellent enantioselectivities (up to 98%) in allylic alkylation.^{3g} Moreover, good results have been obtained in the enantioselective hydrogenation of acrylic acid derivatives, at 1 bar H₂ and 20 °C, using iridium cationic complexes with dithioether ligands.^{3k,l}

Although several reports into the use of chiral dithioethers have been published,^{3i–l,4} hardly any detailed NMR studies of organometallic complexes with this type of ligands have been carried out.⁵ A feature of complexes containing chiral thioether/dithioether ligands is that the sulfur atoms, which become stereogenic centres upon co-ordination, can invert readily in solution at ambient temperature and give mixtures of diastereomers. Moreover, different conformations of the chelate ring can be obtained. These two factors could reduce the effectiveness of these kinds of ligands in enantioselective catalysis. The number of diastereomers and conformers proved to be determining factors in the efficiency and stereoselectivity of the catalytic reactions. The incorporation of C₂ symmetry into a chiral ligand is a well recognised strategy for restricting the number of diastereomers. Recent studies, however, have shown that C₁ dithioether donor ligands are advantageous in some cases.^{3k,l}

In this context we have developed the synthesis of different families of dithioether ligands with a different symmetry

and rigidity in the backbone.^{3j–l} Using the chiral diphosphine (+)-DIOP [3,4-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane] as a model, we first prepared the related C₂-symmetry dithioether ligands diosR₂ (R = Me, Prⁱ or Ph) (Scheme 1).^{3j} More recently we described the synthesis and



Scheme 1

application of a more rigid and efficient family of dithioether C₁-symmetry degusR₂ ligands (R = Me, Prⁱ or Ph).^{3k} To direct our research to obtain further information on the stability and stereochemistry of some potential catalyst precursors, we report the preparation of new complexes of Pd^{II} and Pt^{II} with these two families of chiral dithioether ligands and investigate their co-ordination chemistry in detail.

Results and discussion

Preparation of the complexes

The palladium complexes [PdCl₂(degusR₂)] (R = Me, Prⁱ or Ph) and [PdCl₂(diosR₂)] (R = Me or Prⁱ) were obtained by treating [PdCl₂(PhCN)₂] with an equimolar amount of the corresponding dithioether ligands in methylene chloride (Scheme 2). The dithioether ligand diosPh₂ did not react with [PdCl₂(PhCN)₂] under these conditions.

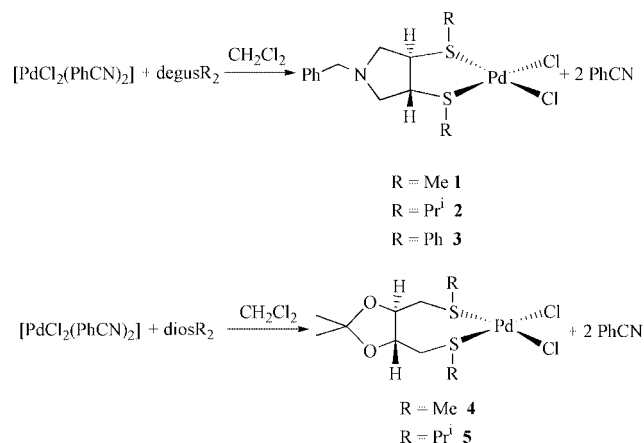
When the experiments were carried out with the corresponding platinum complex [PtCl₂(PhCN)₂] no reaction was observed. However, the reaction of the corresponding dithioethers degusR₂ (R = Me, Prⁱ or Ph) and diosR₂ (R = Me or Prⁱ) with [PtCl₂(cod)] in the presence of AgBF₄ in dichloromethane solution proceeded with displacement of the chloro ligands to yield the cationic complexes [Pt(cod)(degusR₂)] [BF₄]₂ and

[Pt(cod)(diosR₂)] [BF₄]₂, respectively (Scheme 3). Complex [PtCl₂-(cod)] did not react with diosPh₂ under these conditions.

The palladium and platinum complexes **1–10** were isolated by precipitation from hexane and diethyl ether as air stable solids. In solution all the palladium complexes **1–5** and the platinum complexes **9, 10** were stable. Platinum complexes **6–8** were unstable in solution, even under a nitrogen atmosphere and could be characterised only in the solid state. Elemental analysis of C, H and S is consistent with the stoichiometry [PdCl₂(S-S)]_n and [Pt(cod)(S-S)]_n[BF₄]_{2n} (S-S = degusR₂ or diosR₂). The mass spectra show that the palladium complexes **1–5** have their highest ions at *m/z* values corresponding to the loss of two Cl⁻ in the molecular species. Platinum complexes **6–10** have their highest ions at values corresponding to the expected loss of BF₄⁻ anions (see Experimental section). For **6–10** the IR spectra show a strong band between 1090 and 1050 cm⁻¹ and a medium band at 450 cm⁻¹. These are characteristic of non-co-ordinated BF₄⁻ anion in cationic complexes.⁶

The structure of complexes [PdCl₂(S-S)] and [Pt(cod)(S-S)]²⁺ may be revealed by ¹H and ¹³C NMR spectroscopy. The data for **4, 5** and **10** were assigned using COSY spectra and Distortionless Enhancement of Polarisation Transfer (DEPT) spectra. For complexes **1–3**, Heteronuclear Correlation Spectroscopy (HETCOR) was also necessary to assign the signals.

As mentioned previously, dithioether ligands create two stereogenic centres when they co-ordinate. Several stereoisomers with different spatial arrangements of the S-R substituents can be obtained (Fig. 1). In the case of ligands degusR₂, which present C₁ symmetry, four diastereomers can therefore be formed. Since degusR₂ ligands have an (*R,R*) configuration, the four possible diastereomers are *RRRR*, *RRSS*, *RRRS* and *RRSR*. Diastereomers *RRRR* and *RRSS* correspond to the *anti* invertomers and *RRRS* and *RRSR* to the *syn* isomers.



Scheme 2

the *syn*. Three diastereomers can be revealed with the C₂ symmetry (*S,S*) diosR₂ ligands: *SSRR*, *SSSS* both attributed to the *anti* isomers and *SSRS* or *SSSR* corresponding to *syn* isomers.

Complexes with C₁ symmetric degusR₂ ligands

For complexes **1** and **3** the ¹H and ¹³C NMR data indicate the presence of two isomers (denoted as **a** and **b**) in ratio 2:1. For **2** only one diastereomer is detected (Table 1). For all these complexes the shape of their NMR spectra is not affected when the sample is cooled to -90 °C and heated to 40 °C. This fact suggests that there is no interconversion between diastereomers on the NMR timescale at room temperature. Therefore, for **1** and **3**, each ¹H NMR spectrum shows four doublets of two different intensities (ratio 2:1) corresponding to the benzyl protons (CH₂Ph) of the major and minor diastereomers, respectively (Table 1). As expected for these groups, the ¹³C NMR spectra show two signals of different intensities at δ 61.8 and 62.2 for the diastereomers of complex **1** and at δ 62.4 and 62.8 for those of **3**. Four signals of two different intensities in a ratio of 2:1 are also observed for the CH groups in the ¹H and ¹³C NMR. This is also observed for the pyrrolidine methylene signals in the ¹³C NMR spectra. In the ¹H and ¹³C NMR spectra the SMe groups are non-equivalent and show four signals of two different intensities (ratio 2:1) attributed to diastereomers **1a** and **1b**, respectively. The aromatic protons from the PhS groups of complexes **3a** and **3b** have been assigned on the basis of selective decoupling and NOE experiments (Table 2). So, for example, the *ortho*-protons of the major isomer **3a** appear as two doublets at δ 7.40 and 7.70, while the corresponding resonances for minor isomer **3b** appear at δ 6.80 and 7.91.

For the major isomer **3a**, irradiation of the CH resonances at δ 3.11 and 4.36 causes a significant NOE enhancement of the *ortho*-protons of the SPh group at δ 7.40 and 7.70, respectively (Fig. 2). This is consistent with an axial-axial location of the SPh groups in the *anti* *RRRR* configuration or with a pseudo

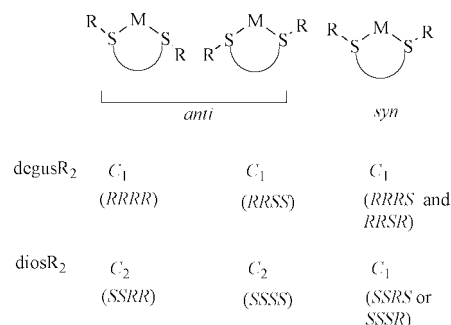
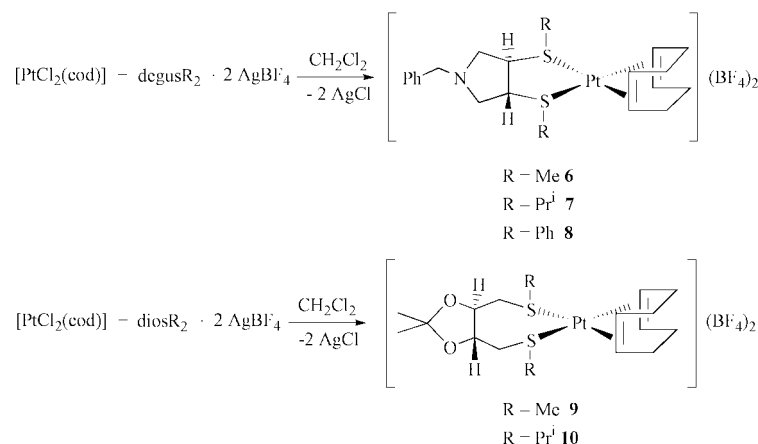


Fig. 1 Possible diastereomers for complexes **1–10**.



Scheme 3

Table 1 The NMR spectroscopic data for compounds **1a**, **1b**, **2**, **3a** and **3b**^a

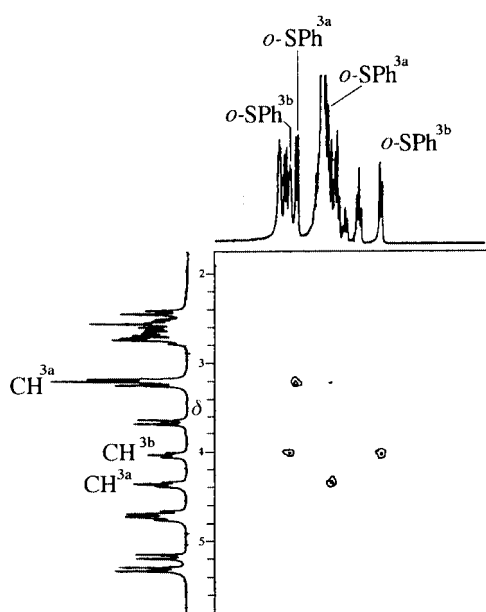
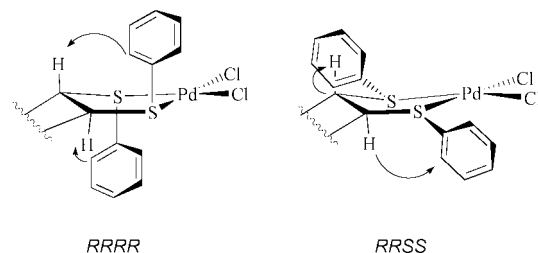
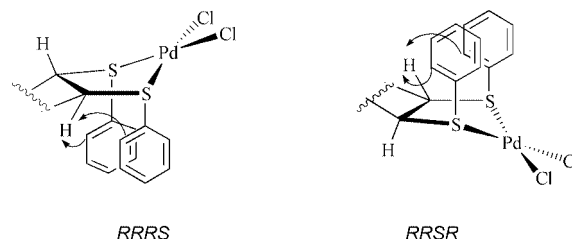
Compound	CH ₂ Ph	CH ₂ N	CH	SMe	SCH	Me
¹ H						
1a	3.51 (d) ^b 5.17 (d)	2.39 (m) 4.56 (m) 4.45 (m)	3.22 (m) 4.15 (m)	2.21 (s) 2.62 (s)		
1b	4.00 (d) ^c 5.03 (d)	2.15 (b) 2.41 (m) 4.68 (m)	3.12 (b) 3.42 (b)	2.50 (s) 2.81 (s)		
2	3.49 (d) ^d 5.30 (d)	2.45 (m) 2.55 (m) 2.95 (m) 4.71 (m)	3.05 (m) 3.72 (m)		3.05 (m) 3.85 (m)	1.35 (d) ^e 1.42 (d) 1.55 (d) 1.82 (d)
3a	3.24(d) ^f 5.39 (d)	2.30–2.80 (m) 4.78 (m)	3.11 (m) 4.36 (m)			
3b	3.63 (d) ^g 5.26 (d)	2.30–2.80 (m) 4.78 (m)	3.19 (m) 4.03 (m)			
¹³ C						
1a	61.8	62.7 63.7	45.4 49.8	15.7 19.2		
1b	62.2	62.4 62.8	47.2 50.5	20.7 23.1		
2	63.0	65.0 66.0	45.9 51.8		38.0 44.0	23.5 23.9 24.5 24.8
3a	62.4	65.1 63.3	47.3 55.4			
3a	62.8	62.2 61.1	46.4 53.5			

^aCDCl₃ solvent. Chemical shifts in ppm with SiMe₄ as internal standard, coupling constants in Hz; room temperature. Abbreviations: s, singlet; m, multiplet; d, doublet; b, broad. ^{b2}J_{H-H} = 15. ^{c2}J_{H-H} = 14. ^{d2}J_{H-H} = 11.5. ^{e3}J_{H-H} = 7.2. ^{f2}J_{H-H} = 13.1. ^{g2}J_{H-H} = 12.1.

Table 2 Selected ¹H NMR data for the SPh part for compounds **3a** and **3b**^a

Compound	<i>o</i>	<i>m</i>	<i>p</i>
3a	7.40 (d) ^b 7.70 (d)	7.30 (t) ^c 7.40 (m)	7.40 (m) 7.82 (m)
3b	6.80 (d) ^d 7.91 (d)	7.05 (t) ^e 7.38 (t)	7.20 (t) ^f 7.54 (t)

^aCDCl₃ solvent. Chemical shifts in ppm, coupling constants in Hz; room temperature. Abbreviations: *o*, *ortho*; *m*, *meta*; *p*, *para*; d, doublet; m, multiplet; t, triplet. ^{b3}J_{H-H} = 7.4. ^{c3}J_{H-H} = 7.5. ^{d3}J_{H-H} = 7.4. ^{e3}J_{H-H} = 7.5. ^{f3}J_{H-H} = 7.5.

**Fig. 2** Section of the NOESY spectrum of diastereomers **3a** and **3b**.**Fig. 3** Representation of the two possible *syn* diastereomers for complex **3a**. The arrows show the cross peak signals.**Fig. 4** Representation of the two possible *syn* diastereomers with the dithioether groups located in an axial position for complex **3b**. The arrows show the cross peak signals.

equatorial–equatorial disposition of the SPh groups in the *anti* *RRSS* configuration (Fig. 3). On the other hand, when the signal of the CH groups of the minor isomer **3b** at δ 4.03 is under irradiation, the resonances of the *ortho*-protons of the SPh groups at δ 6.80 and 7.91 simultaneously experience NOE (Fig. 2). This is in accord with a *syn* axial–axial position of both phenyl groups. Fig. 4 shows the two possible diastereomers, *RRRS* and *RRSR*, with the thioether substituents located in axial positions where the five-membered chelate ring adopts an envelope conformation.

For isomer **1a**, irradiation of the signal of the CH group at δ 4.15 causes a significant NOE enhancement of the methyl

Table 3 Selected NMR spectroscopic data for complexes **4a**, **4b**, **5**, **9** and **10**^a

Compound	cod		Dithioether						
	CH ₂	CH=CH	CMe	CH	CH ₂	SCH	Me	SMe	CMe
¹ H									
4a			1.40 (s)	4.60 (t) ^b	3.40 (m)			2.44 (s)	
4b			1.40 (s)	4.70 (m)	3.10 (b)			1.58 (s)	
				4.90 (m)				2.51 (s)	
5			1.40 (s)	4.30 (m)	3.00 (m)	3.60 (sp) ^c	1.50 (d) ^d		
					3.50 (m)		1.56 (d)		
9	2.40 (m)	5.50 (b)	1.40 (s)	4.15 (m)	3.20 (m)			2.80 (b)	
	2.60 (m)	6.20 (b)			3.40 (m)				
10	2.50 (m)	5.50 (m)	1.50 (s)	4.10 (m)	3.05 (dd) H _{ax} ^e	3.40 (m)			
	2.75 (m)	6.20 (m)			3.15 (dd) H _{eq} ^f				
¹³ C									
4a			27.1	78.4	40.0			22.2	111.1
4b				27.1	78.8 (b)	40.3 (b)		21.8 (b)	111.2
5			27.1	77.6	42.9	34.8	22.3		109.9
							22.4		
10	29.4	76.1	27.1	78.1	39.9	36.1	21.0		110.1
	33.4	80.6					22.7		

^aChemical shifts in ppm, coupling constants in Hz; room temperature. In CDCl₃ solvent. Abbreviations: s, singlet; m, multiplet; d, doublet; t, triplet; dd, double doublet; sp, septuplet; b, broad. ^{b3}J_{H-H} = 5.2. ^{c3}J_{H-H} = 3.2. ^{d3}J_{H-H} = 3.2. ^{e2}J_{gem} = 13.0, ³J_{ax-ax} = 7.5. ^{f2}J_{gem} = 13.0, ³J_{eq-ax} = 3.2.

groups at δ 2.62, which is consistent with an axial position for this thioether substituent. On the other hand, the NOE experiment suggests that the methyl group at δ 2.21 is in an equatorial position. These data indicate an axial–equatorial disposition of the methyl substituents. The NOE experiments for the minor isomer **1b** are also in accord with an axial–equatorial location for the methyl groups at δ 2.81 and 2.50, respectively. For **2** the ¹H and ¹³C NMR spectra agree with the expected pattern for this complex with a C₁ ligand. The ¹³C NMR spectrum shows two signals for the two secondary carbons of the CH₂N group, two for the methinic carbons of the SCH groups and two for the CH groups. Four signals for the Me groups are observed in the ¹³C and ¹H NMR spectra. The VT-NMR data indicate that there is only one isomer. As with isomers **1a** and **1b**, the NOE experiments are consistent with an axial–equatorial location for the isopropyl groups at δ 3.72 and 3.05, respectively.

Complexes with C₂ symmetric diosR₂ ligands

The ¹H and ¹³C NMR spectra of palladium complex **4** indicate that two diastereomers (denoted as **4a** and **4b**) are present in solution at room temperature in a ratio of 3:2 (Table 3). For diastereomer **4a** the NMR data are consistent with a C₂ symmetry. The SMe and the methinic protons appear at δ 2.44 and at 4.60, respectively, and do not show any splitting on lowering the temperature. However, for the minor isomer **4b**, the NMR spectra show a C₁ symmetry pattern: two singlets at δ 2.51 and 1.58 are observed for the inequivalent methyl substituents of the dithioether. The inequivalent methinic protons also appear as two multiplets at δ 4.70 and 4.90. For all complexes, there were no changes in the variable temperature NMR spectra from –90 to 40 °C.

For isomer **4a** the NOE experiments are in accord with an equatorial–equatorial location for the methyl groups. Fig. 5 shows the two possible C₂-symmetrical diastereomers, SSRR and SSSS, with the thioether substituents located in equatorial positions. The SSRR isomer has the seven-membered chelate ring in a twisted-chair conformation while diastereomer SSSS presents a boat conformation of the chelate ring. Examination of models suggests a preference for the SSRR isomer, since its chair-twisted accommodation is less hindered than the puckered conformation SSSS. For the minor isomer **4b**, when the methyl signal at δ 1.58 is irradiated, cross peaks with one

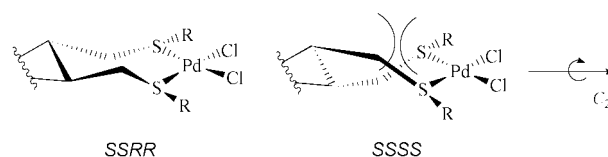


Fig. 5 Representation of the two possible *anti* diastereomers for complex **4a** with the dithioether groups located in equatorial position.

of the two methinic groups and the methylenic groups are observed. This is consistent with an axial disposition of this SMe group. The NOE experiment also indicates that the less-shielded methyl resonance belongs to an equatorial position. From these data, the minor isomer **4b** can be assigned to an axial–equatorial disposition of the methyl substituents.

The ¹H NMR data (Table 3) show that platinum complex **9** is fluxional in solution at room temperature. The spectrum therefore shows two broad signals (4H) at δ 5.50 and 6.20, two multiplets (8H) at δ 2.40 and 2.60 and a broad signal (6H) at δ 2.80 for the SMe protons. The first two resonances are attributed to the olefinic protons of the co-ordinated cyclooctadiene and the next two resonances correspond to its methylene protons. The shape of the NMR spectrum is not affected when the sample is cooled to –90 °C. In particular, the methyl resonance at δ 2.80 does not show any splitting, which indicates a mixture of diastereomers having fluxional behaviour.

The VT-NMR spectra of complexes **5** and **10** show only one C₂ symmetry diastereomer in solution. This follows from the NMR data (see Table 3). In particular, we can see that (i) the two CH groups are equivalent *i.e.* there is only one signal in ¹H and ¹³C NMR; (ii) in the ¹H NMR spectrum of **10** the diastereotopic methylenic protons appear as two doublets of doublets, which correspond to H_{ax} (*J*_{gem} = 13.0, *J*_{ax-ax} = 7.5 Hz) and H_{eq} (*J*_{gem} = 13.0, *J*_{eq-ax} = 3.2 Hz), respectively. For complex **5** these methylenic protons appear as two multiplets, which cannot be resolved by changing temperature. There is only one signal in the ¹³C NMR spectrum for the two secondary carbons; (iii) the two isopropyl groups are equivalent, since in the ¹³C NMR spectrum there are only three signals for these groups. For complexes **5** and **10** the NOE experiments are consistent with an equatorial disposition of the isopropyl groups. In summary, all the NMR data suggest that for **5** and **10** there is only one diastereoisomer, which could be the *anti*-SSRR.

As expected, for complexes containing diosR₂ ligands, the equatorial disposition of the dithioether groups is preferred. This is not the case for **1–3**, where the rigidity of the backbone ligand allows other structures whose thioether substituents are located in an axial–axial or equatorial–axial position. Moreover, for **3b** the unusual stabilisation of the *syn* axial–axial disposition may be explained by the π -stacking interaction between the two parallel phenyl groups. Surprisingly, complexes **4** and **10**, which contain a less rigid backbone ligand, did not show a fluxional process over the range of temperature scanned, unlike complexes of Pd and Pt containing related chiral C₂ methyl dithioether ligands derived from 1,1'-binaphthalene-2,2'-dithiol (BINAS) which are all fluxional in solution at room temperature.⁵

Conclusion

The palladium complexes **1**, **3**, **4** and the platinum complex **10** reported here show a mixture of two diastereomers in solution at room temperature. VT-NMR indicates that no interconversion between diastereomers takes place at room temperature. Only complex [Pt(cod)(diosMe₂)](BF₄)₂ is extremely fluxional and its diastereomers did not show any isolated NMR resonances even at –90 °C. Moreover, only one diastereomer was observed for complexes [PdCl₂{(–)-degusPrⁱ₂}] **2**, [PdCl₂{(–)-diosPrⁱ₂}] **5** and [Pt(cod){(–)-diosPrⁱ₂}](BF₄)₂ **10**, which contain the more hindered ligands degusPrⁱ₂ and diosPrⁱ₂. This result could indicate that complexes with diosPrⁱ₂ and degusPrⁱ₂ are well suited for use in enantioselective catalysis. The promising results encouraged us to test the catalyst precursors in enantioselective catalysis. The preliminary results are consistent with the conclusions of this paper and will be presented extensively in future.

Experimental

General comments

Elemental analyses were carried out with a Carlo-Erba micro-analyzer. Infrared spectra were recorded on a Midac Grams/386 spectrophotometer, ¹H and ¹³C NMR spectra on a Varian Gemini 300 MHz. Standard-pulse sequences were employed for ¹H-NOE⁷ and ¹H-2-D-NOESY.⁸ The phase-sensitive NOESY experiments used mixing times of 0.4 s. FAB mass spectrometry was performed on a VG autospect in a 3-nitrobenzyl alcohol matrix. All the platinum complexes were synthesized using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled and deoxygenated before use. Complexes [PdCl₂(PhCN)₂]⁹ and [PtCl₂(cod)]¹⁰ and the dithioethers degusR₂^{3k} and diosR₂^{3j} (R = Me, Prⁱ or Ph) were prepared using reported methods. All other reagents were used as commercially supplied.

Synthesis of the complexes

[PdCl₂{(–)-degusMe₂}] **1**. The ligand (–)-degusMe₂ (27 mg, 0.1 mmol) was added to a solution of [PdCl₂(PhCN)₂] (40 mg, 0.1 mmol) in dichloromethane (5 ml). After stirring at room temperature for 30 min hexane was added to give a yellow precipitate of complex **1** which was filtered off, washed with cold hexane and dried in vacuum (42 mg, 92%) (Found: C, 36.20; H, 4.55; N, 3.20; S, 14.97. Calc. for C₁₃H₁₉Cl₂NPdS₂: C, 36.26; H, 4.45; N, 3.25; S, 14.86%; *m/z* 358 (M – 2Cl[–]).

[PdCl₂{(–)-degusPrⁱ₂}] **2**. The procedure described for compound **1** was used. This produced 46 mg (90%) (Found: C, 41.85; H, 5.70; N, 2.89; S, 13.62. Calc. for C₁₇H₂₇Cl₂NPdS₂: C, 41.94; H, 5.60; N, 2.89; S, 13.70%; *m/z* 414 (M – 2Cl[–]).

[PdCl₂{(+)-degusPh₂}] **3**. The procedure described for compound **1** was used. This produced 61 mg (95%) (Found: C, 49.78;

H, 4.20; N, 2.57; S, 10.89. Calc. for C₂₃H₂₃Cl₂NPdS₂: C, 49.79; H, 4.18; N, 2.52; S, 11.05%; *m/z* 482 (M – 2Cl[–]).

[PdCl₂{(–)-diosMe₂}] **4**. The ligand (–)-diosMe₂ (22 mg, 0.1 mmol) was added to a solution of [PdCl₂(PhCN)₂] (40 mg, 0.1 mmol) in dichloromethane (5 ml). After stirring at room temperature for 30 min hexane was added to give a yellow precipitate of **4** which was filtered off, washed with cold hexane and dried in vacuum (36 mg, 90%) (Found: C, 27.04; H, 4.59; S, 16.24. Calc. for C₉H₁₈Cl₂O₂PdS₂: C, 27.04; H, 4.54; S, 16.04%; *m/z* 327 (M – 2Cl[–]).

[PdCl₂{(–)-diosPrⁱ₂}] **5**. The procedure described for the previous compound was used. This produced 45 mg (95%) (Found: C, 34.30; H, 5.65; S, 14.09. Calc. for C₁₃H₂₆Cl₂O₂PdS₂: C, 34.20; H, 5.70; S, 14.07%; *m/z* 383 (M – 2Cl[–]).

[Pt(cod){(–)-degusMe₂}](BF₄)₂ **6**. The stoichiometric amount of the ligand (–)-degusMe₂ (27 mg, 0.1 mmol) and AgBF₄ (19 mg, 0.1 mmol) was added to a dichloromethane solution (3 ml) of [PtCl₂(cod)] (37 mg, 0.1 mmol) to produce a white precipitate of silver chloride, which was filtered off through Kieselguhr. Adding diethyl ether to the filtrate precipitated the required complex **6** as a white solid. This was filtered off, washed with cold diethyl ether and vacuum dried (53 mg, 68%) (Found: C, 35.02; H, 4.05; N, 2.02; S, 9.07. Calc. for C₂₁H₃₁B₂F₈NPtS₂: C, 34.54; H, 4.28; N, 1.92; S, 8.78%; *m/z* 556 (M – 2BF₄[–]).

[Pt(cod){(–)-degusPrⁱ₂}](BF₄)₂ **7**. The procedure described for the previous compound was used. This produced 65 mg (72%) (Found: C, 38.14; H, 5.16; N, 1.79; S, 8.56. Calc. for C₂₅H₃₉B₂F₈NPtS₂: C, 38.19; H, 5.00; N, 1.78; S, 8.15%; *m/z* 613 (M – 2BF₄[–]).

[Pt(cod){(–)-degusPh₂}](BF₄)₂ **8**. The procedure described for compound **6** was used. This produced 74 mg (80%) (Found: C, 43.30; H, 4.18; N, 1.60; S, 7.46. Calc. for C₃₁H₃₅B₂F₈NPtS₂: C, 43.58; H, 4.13; N, 1.64; S, 7.50%; *m/z* 680 (M – 2BF₄[–]).

[Pt(cod){(–)-diosMe₂}](BF₄)₂ **9**. The stoichiometric amount of the ligand (–)-diosMe₂ (22 mg, 0.1 mmol) and AgBF₄ (19 mg, 0.1 mmol) was added to a dichloromethane solution (3 ml) of [PtCl₂(cod)] (37 mg, 0.1 mmol) to produce a white precipitate of silver chloride, which was filtered off through Kieselguhr. Adding diethyl ether to the filtrate precipitated complex **9** as a white solid, which was filtered off, washed with cold diethyl ether and vacuum dried (50 mg, 67%) (Found: C, 29.35; H, 4.40; S, 9.17. Calc. for C₁₇H₃₀B₂F₈O₂PtS₂: C, 29.20; H, 4.30; S, 8.72%; *m/z* 524 (M – 2BF₄[–]).

[Pt(cod){(–)-diosPrⁱ₂}](BF₄)₂ **10**. The procedure described for the previous compound was used. This produced 56 mg (71%) (Found: C, 33.95; H, 5.32; S, 8.77. Calc. for C₂₁H₃₈B₂F₈O₂PtS₂: C, 33.39; H, 5.07; S, 8.49%; *m/z* 580 (M – 2BF₄[–]).

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