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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 (−)-degusMe$_2$, (−)-1-benzyl-3,4-bis(isopropylsulfanyl)pyrrolidine (−)-degusPr$^i_2$, (+)-1-benzyl-3,4-bis(phenylsulfanyl)pyrrolidine (+)-degusPh$_2$, (−)-2,2-dimethyl-4,5-bis(methylsulfanylmethyl)-1,3-dioxolane (−)-diosMe$_2$ and (−)-4,5-bis(isopropylsulfanylmethyl)-2,2-dimethyl-1,3-dioxolane (−)-diosPr$^i_2$, have been prepared and characterised by NMR. The complexes [PdCl$_2${(−)-degusMe$_2$}], [PdCl$_2${(+)-degusPh$_2$}] and [PdCl$_2${(−)-diosMe$_2$}] 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){(−)-diosMe$_2$}][BF$_4$]$_2$ is extremely fluxional and its diastereomers did not show isolated NMR resonances even at −90 °C. The complexes [PdCl$_2${(−)-degusPr$^i_2$}], [PdCl$_2${(−)-diosPr$^i_2$}] and [Pt(cod){(−)-diosPr$^i_2$}][BF$_4$]$_2$, 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 H_2 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 C_2 symmetry into a chiral ligand is a well recognised strategy for restricting the number of diastereomers. Recent studies, however, have shown that C_1 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 C_2-symmetry dithioether ligands diosR$_2$ (R = Me, Pr^i or Ph) (Scheme 1).[3j] More recently we described the synthesis and

diosR$_2$ R = Me, Pr^i, Ph degusR$_2$ R = Me, Pr^i, Ph

Scheme 1

application of a more rigid and efficient family of dithioether C_1-symmetry degusR$_2$ ligands (R = Me, Pr^i 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 [PdCl$_2$(degusR$_2$)] (R = Me, Pr^i or Ph) and [PdCl$_2$(diosR$_2$)] (R = Me or Pr^i) were obtained by treating [PdCl$_2$(PhCN)$_2$] with an equimolar amount of the corresponding dithioether ligands in methylene chloride (Scheme 2). The dithioether ligand diosPh$_2$ did not react with [PdCl$_2$(PhCN)$_2$] under these conditions.

When the experiments were carried out with the corresponding platinum complex [PtCl$_2$(PhCN)$_2$] no reaction was observed. However, the reaction of the corresponding dithioethers degusR$_2$ (R = Me, Pr^i or Ph) and diosR$_2$ (R = Me or Pr^i) with [PtCl$_2$(cod)] in the presence of AgBF$_4$ in dichloromethane solution proceeded with displacement of the chloro ligands to yield the cationic complexes [Pt(cod)(degusR$_2$)][BF$_4$]$_2$ and

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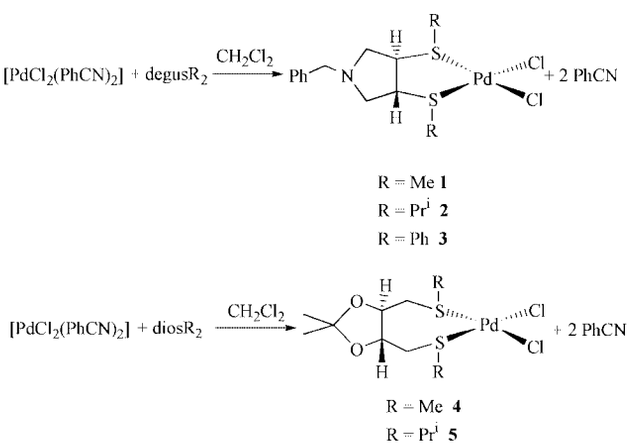
$[Pt(cod)(diosR_2)][BF_4]_2$, respectively (Scheme 3). Complex $[PtCl_2(cod)]$ did not react with $diosPh_2$ under these conditions.

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 $[PdCl_2(S–S)]_n$ and $[Pt(cod)(S–S)]_n[BF_4]_{2n}$ (S–S = $degusR_2$ or $diosR_2$). 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 BF_4^- 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 BF_4^- anion in cationic complexes.[6]

The structure of complexes $[PdCl_2(S–S)]$ and $[Pt(cod)(S–S)]^{2+}$ may be revealed by ^1H and ^{13}C 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 $degusR_2$, which present C_1 symmetry, four diastereomers can therefore be formed. Since $degusR_2$ 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*. Three diastereomers can be revealed with the C_2 symmetry (*S*,*S*) $diosR_2$ ligands: *SSRR*, *SSSS* both attributed to the *anti* isomers and *SSRS* or *SSSR* corresponding to *syn* isomers.



Scheme 2

Complexes with C_1 symmetric $degusR_2$ ligands

For complexes **1** and **3** the ^1H and ^{13}C 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 (CH_2Ph) of the major and minor diastereomers, respectively (Table 1). As expected for these groups, the ^{13}C 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 ^{13}C NMR. This is also observed for the pyrrolidine methylene signals in the ^{13}C NMR spectra. In the ^1H and ^{13}C 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

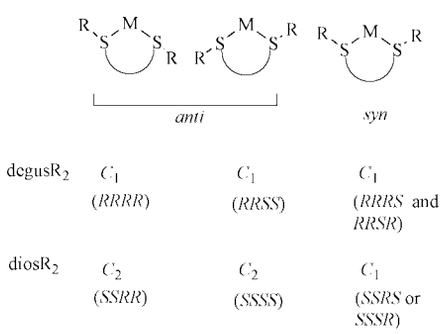
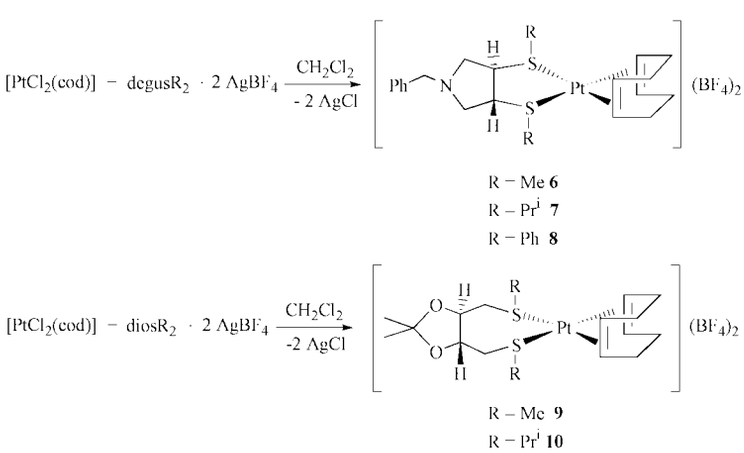


Fig. 1 Possible diastereomers for complexes **1**–**10**.



Scheme 3

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

Compound	CH_2Ph	CH_2N	CH	SMe	SCH	Me
^1H						
1a	3.51 (d)[b]	2.39 (m)	3.22 (m)	2.21 (s)		
	5.17 (d)	4.56 (m)	4.15 (m)	2.62 (s)		
		4.45 (m)				
1b	4.00 (d)[c]	2.15 (b)	3.12 (b)	2.50 (s)		
	5.03 (d)	2.41 (m)	3.42 (b)	2.81 (s)		
		4.68 (m)				
2	3.49 (d)[d]	2.45 (m)	3.05 (m)		3.05 (m)	1.35 (d)[e]
	5.30 (d)	2.55 (m)	3.72 (m)		3.85 (m)	1.42 (d)
		2.95 (m)				1.55 (d)
		4.71 (m)				1.82 (d)
3a	3.24(d)[f]	2.30–2.80 (m)	3.11 (m)			
	5.39 (d)	4.78 (m)	4.36 (m)			
3b	3.63 (d)[g]	2.30–2.80 (m)	3.19 (m)			
	5.26 (d)	4.78 (m)	4.03 (m)			
^{13}C						
1a	61.8	62.7	45.4	15.7		
		63.7	49.8	19.2		
1b	62.2	62.4	47.2	20.7		
		62.8	50.5	23.1		
2	63.0	65.0	45.9		38.0	23.5
		66.0	51.8		44.0	23.9
						24.5
						24.8
3a	62.4	65.1	47.3			
		63.3	55.4			
3a	62.8	62.2	46.4			
		61.1	53.5			

[a] $CDCl_3$ solvent. Chemical shifts in ppm with $SiMe_4$ as internal standard, coupling constants in Hz; room temperature. Abbreviations: s, singlet; m, multiplet; d, doublet; b, broad. [b] $^2J_{H\text{-}H} = 15$. [c] $^2J_{H\text{-}H} = 14$. [d] $^2J_{H\text{-}H} = 11.5$. [e] $^3J_{H\text{-}H} = 7.2$. [f] $^2J_{H\text{-}H} = 13.1$. [g] $^2J_{H\text{-}H} = 12.1$.

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

Compound	*o*	*m*	*p*
3a	7.40 (d)[b]	7.30 (t)[c]	7.40 (m)
	7.70 (d)	7.40 (m)	7.82 (m)
3b	6.80 (d)[d]	7.05 (t)[e]	7.20 (t)[f]
	7.91 (d)	7.38 (t)	7.54 (t)

[a] $CDCl_3$ solvent. Chemical shifts in ppm, coupling constants in Hz; room temperature. Abbreviations: *o*, *ortho*; *m*, *meta*; *p*, *para*; d, doublet; m, multiplet; t, triplet. [b] $^3J_{H\text{-}H} = 7.4$. [c] $^3J_{H\text{-}H} = 7.5$. [d] $^3J_{H\text{-}H} = 7.4$. [e] $^3J_{H\text{-}H} = 7.5$. [f] $^3J_{H\text{-}H} = 7.5$.

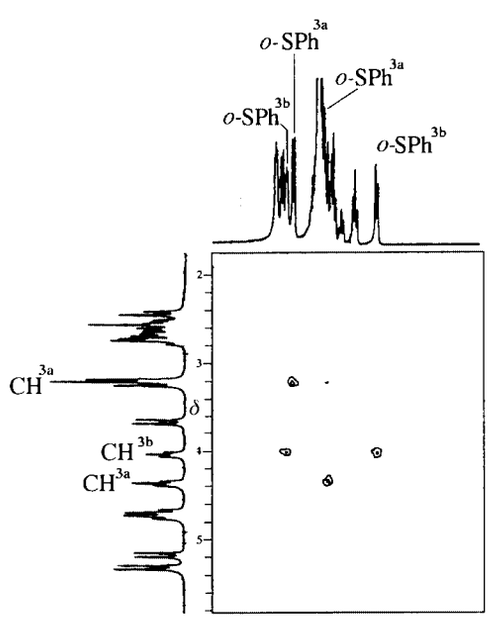


Fig. 2 Section of the NOESY spectrum of diastereomers **3a** and **3b**.

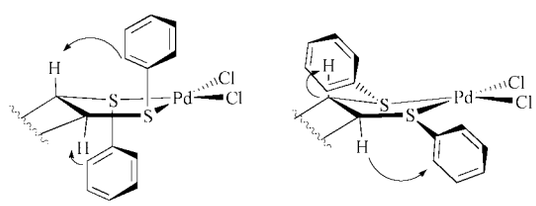


Fig. 3 Representation of the two possible *syn* diastereomers for complex **3a**. The arrows show the cross peak signals.

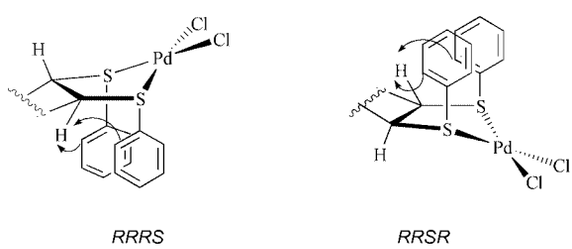


Fig. 4 Representation of the two possible *syn* diastereomers with the dithioether groups located in an axial position for complex **3b**. The arrows show the cross peak signals.

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]

	cod		Dithioether						
Compound	CH_2	CH=CH	C*Me*	CH	CH_2	SCH	Me	SMe	*C*Me
^{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		

[a] Chemical shifts in ppm, coupling constants in Hz; room temperature. In $CDCl_2$ solvent. Abbreviations: s, singlet; m, multiplet; d, doublet; t, triplet; dd, double doublet; sp, septuplet; b, broad. [b] $^3J_{H\text{-}H}$ = 5.2. [c] $^3J_{H\text{-}H}$ = 3.2. [d] $^3J_{H\text{-}H}$ = 3.2. [e] $^2J_{gem}$ = 13.0, $^3J_{ax\text{-}ax}$ = 7.5. [f] $^2J_{gem}$ = 13.0, $^3J_{eq\text{-}ax}$ = 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 ^{1}H and ^{13}C NMR spectra agree with the expected pattern for this complex with a C_1 ligand. The ^{13}C NMR spectrum shows two signals for the two secondary carbons of the CH_2N 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 ^{13}C and ^{1}H 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 C_2 symmetric diosR$_2$ ligands

The ^{1}H and ^{13}C 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 C_2 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 C_1 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 C_2-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

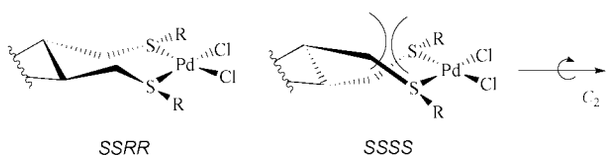


Fig. 5 Representation of the two possible *anti* diastereomers for complex **4a** with the dithioether groups located in equatorial position.

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 ^{1}H 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 C_2 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 ^{1}H and ^{13}C NMR; (ii) in the ^{1}H NMR spectrum of **10** the diastereotopic methylenic protons appear as two doublets of doublets, which correspond to H_{ax} (J_{gem} = 13.0, $J_{ax\text{-}ax}$ = 7.5 Hz) and H_{eq} (J_{gem} = 13.0, $J_{eq\text{-}ax}$ = 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 ^{13}C NMR spectrum for the two secondary carbons; (iii) the two isopropyl groups are equivalent, since in the ^{13}C 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 diosR$_2$ 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 C_2 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)(diosMe$_2$)][BF$_4$]$_2$ 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 [PdCl$_2${(−)-degusPr$^i_2$}] **2**, [PdCl$_2${(−)-diosPr$^i_2$}] **5** and [Pt(cod){(−)-diosPr$^i_2$}][BF$_4$]$_2$ **10**, which contain the more hindered ligands degusPr$^i_2$ and diosPr$^i_2$. This result could indicate that complexes with diosPr$^i_2$ and degusPr$^i_2$ 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 microanalyzer. Infrared spectra were recorded on a Midac Grams/386 spectrophotometer, ^{1}H and ^{13}C NMR spectra on a Varian Gemini 300 MHz. Standard-pulse sequences were employed for ^{1}H-NOE[7] and ^{1}H-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 [PdCl$_2$(PhCN)$_2$][9] and [PtCl$_2$(cod)][10] and the dithioethers degusR$_2$[3k] and diosR$_2$[3j] (R = Me, Pr^i or Ph) were prepared using reported methods. All other reagents were used as commercially supplied.

Synthesis of the complexes

[PdCl$_2${(−)-degusMe$_2$}] 1. The ligand (−)-degusMe$_2$ (27 mg, 0.1 mmol) was added to a solution of [PdCl$_2$(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 $C_{13}H_{19}Cl_2NPdS_2$: C, 36.26; H, 4.45; N, 3.25; S, 14.86%); *m*/*z* 358 (M − 2Cl$^-$).

[PdCl$_2${(−)-degusPr$^i_2$}] 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 $C_{17}H_{27}Cl_2NPdS_2$: C, 41.94; H, 5.60; N, 2.89; S, 13.70%); *m*/*z* 414 (M − 2Cl$^-$).

[PdCl$_2${(+)-degusPh$_2$}] 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 $C_{23}H_{23}Cl_2NPdS_2$: C, 49.79; H, 4.18; N, 2.52; S, 11.05%); *m*/*z* 482 (M − 2Cl$^-$).

[PdCl$_2${(−)-diosMe$_2$}] 4. The ligand (−)-diosMe$_2$ (22 mg, 0.1 mmol) was added to a solution of [PdCl$_2$(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 $C_9H_{18}Cl_2O_2PdS_2$: C, 27.04; H, 4.54; S, 16.04%); *m*/*z* 327 (M − 2Cl$^-$).

[PdCl$_2${(−)-diosPr$^i_2$}] 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 $C_{13}H_{26}Cl_2O_2PdS_2$: C, 34.20; H, 5.70; S, 14.07%); *m*/*z* 383 (M − 2Cl$^-$).

[Pt(cod){(−)-degusMe$_2$}][BF$_4$]$_2$ 6. The stoichiometric amount of the ligand (−)-degusMe$_2$ (27 mg, 0.1 mmol) and AgBF$_4$ (19 mg, 0.1 mmol) was added to a dichloromethane solution (3 ml) of [PtCl$_2$(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 $C_{21}H_{31}B_2F_8NPtS_2$: C, 34.54; H, 4.28; N, 1.92; S, 8.78%); *m*/*z* 556 (M − 2BF$_4^-$).

[Pt(cod){(−)-degusPr$^i_2$}][BF$_4$]$_2$ 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 $C_{25}H_{39}B_2F_8NPtS_2$: C, 38.19; H, 5.00; N, 1.78; S, 8.15%); *m*/*z* 613 (M − 2BF$_4^-$).

[Pt(cod){(−)-degusPh$_2$}][BF$_4$]$_2$ 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 $C_{31}H_{35}B_2F_8NPtS_2$: C, 43.58; H, 4.13; N, 1.64; S, 7.50%); *m*/*z* 680 (M − 2BF$_4^-$).

[Pt(cod){(−)-diosMe$_2$}][BF$_4$]$_2$ 9. The stoichiometric amount of the ligand (−)-diosMe$_2$ (22 mg, 0.1 mmol) and AgBF$_4$ (19 mg, 0.1 mmol) was added to a dichloromethane solution (3 ml) of [PtCl$_2$(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 $C_{17}H_{30}B_2F_8O_2PtS_2$: C, 29.20; H, 4.30; S, 8.72%); *m*/*z* 524 (M − 2BF$_4^-$).

[Pt(cod){(−)-diosPr$^i_2$}][BF$_4$]$_2$ 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 $C_{21}H_{38}B_2F_8O_2PtS_2$: C, 33.39; H, 5.07; S, 8.49%); *m*/*z* 580 (M − 2BF$_4^-$).

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