Synthesis, Structure, and Dynamic Behaviour of Transition Metal Chelate Complexes with Atropisomeric Dithioether Ligands

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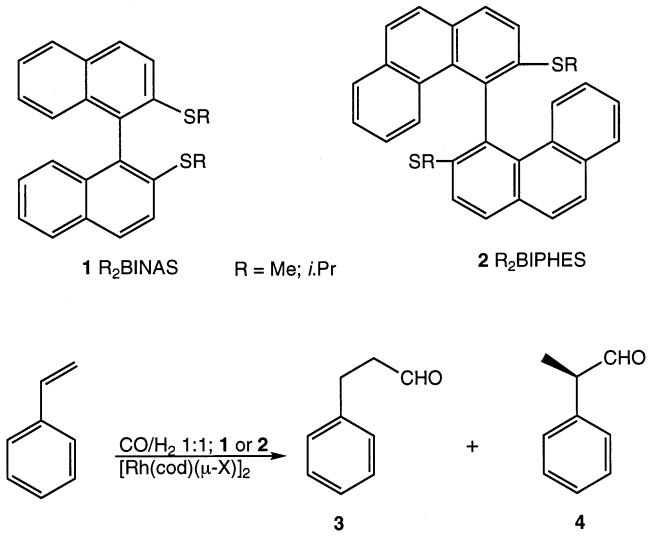
The preparation and characterization of Rh^{I}, Pd^{II}, and Pt^{II} complexes with chiral C_2-symmetrical dithioether ligands derived from 1,1′-binaphthalene-2,2′-dithiol (BINAS) are reported. All complexes are fluxional in solution at room temp. Interconversion between the stereoisomers can take place through conformational equilibration of the chelate ring, and/or inversion of configuration at the stereogenic sulfur. In the solid state the palladium derivative of Me_2BINAS shows a twisted chair conformation of the chelate ring, with both methyl groups in equatorial positions.

Recent investigations by our groups have shown that, in the hydroformylation of styrene[1], rhodium(I) complexes with the atropisomeric dithioethers **1** and **2** (Scheme 1), either preformed or prepared in situ by addition of the appropriate amount of the sulfur donor ligand to a suitable rhodium diolefin precursor $[Rh(cod)(\mu\text{-}X)]_2$ (cod:1,5-cyclooctadiene; X:Cl; MeO), are endowed with a high catalytic activity. Quantitative conversions of the substrate, with complete chemoselectivity in the formation of the aldehydes **3** and **4** (Scheme 1), are easily attained; even at room temp. and for a fairly wide range of carbon monoxide/hydrogen (1:1) pressures.

Scheme 1. Atropisomeric dithioether ligands



As these catalysts favour carbon monoxide insertion into the more substituted vinylic carbon, the major product is the branched isomer **4**, which, in the most favourable cases, can account for more than 95% of the reaction mixture. This regioselectivity, which is among the highest recorded in the hydroformylation of styrene, prompted us to exploit the potential of the enantiopure derivatives **1** and **2** in enantioselective hydroformylation. Transfer of chirality from the ligand to the product does take place, but the efficiency is quite low and the best enantiomeric excess (e.e.) obtained so far is only slightly greater than 20%. Albeit low, this value is in the range of the e.e.′s normally obtained in this reaction after more than twenty years of experimentation using rhodium catalysts containing diphosphane ligands as chiral modifiers[2].

A notable feature of the dithioether ligands **1** and **2** is that upon coordination to the metal they can give rise to different diastereomeric complexes, since the two sulfur donors become stereogenic centers. This fact is expected to

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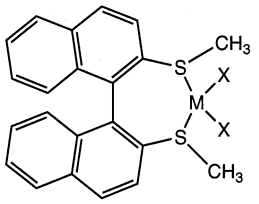
significantly affect the asymmetric bias of enantioselective hydroformylation, as the possibility of matching or mismatching combinations of the original stereogenic element of the ligand, the chiral biaryl backbone, and the newly established stereocenters, can easily be envisaged.

The formation of an unfavourable mixture of diastereomeric rhodium complexes, each one featuring its own stereodifferentiating ability, may well account for the low e.e. obtained in the hydroformylation of styrene. Alternatively this may be due to the configurational lability of the S-stereocenters under hydroformylation conditions.

In order to direct our research in this field on a more rational basis, we were interested to gain further information on the stability and the stereochemistry of the complexes used as catalysts. For this reason we investigated in more detail the coordination chemistry of the atropisomeric dithioethers **1** and **2** with d^8 transition metal centers.

Here we report on the preparation, structure and dynamic behaviour of the cationic and neutral complexes **5**, **6** and **7** obtained from the binaphthyl derivative **1** (R = Me; Me_2BINAS).

Figure 1. Me_2BINAS complexes



5 M = Rh; 2X = 1,5-cyclooctadiene
6 M = Pd; X = Cl
7 M = Pt; X = Cl

Results and Discussion

Preparation of the Complexes: The reaction of **1** with $[Rh(cod)_2]^+X^-$ (X = ClO_4; BF_4) **8** in CH_2Cl_2 solution proceeded, with the displacement of one 1,5-cyclooctadiene ligand, to afford the cationic complexes $[Rh(cod)(Me_2BINAS)]^+X^-$ **5**, isolated in high yield after the addition of diethyl ether. When the reaction was performed in the presence of a moderate excess of ligand **1**, the occasional formation of a byproduct, apparently a rhodium complex containing two units of dithioether ligand, was noticed. This product has not yet been fully characterized.

The chelate Pd complex **6** was obtained by the reaction of $[PdCl_2(PhCN)_2]$ **9** with an equimolar amount of the dithioether **1** in methylene chloride. The complex separated as a red solid upon the addition of diethyl ether. Under these conditions, the corresponding Pt complex $[PtCl_2(PhCN)_2]$ **10** does not react with the ligand **1** at room temp. However under UV irradiation at 254 nm in $CHCl_3$, chelate complexation of the dithioether ligand to the platinum center, with displacement of the ancillary benzonitrile ligands, takes place and is completed in a few hours. Addition of hexane leads to the precipitation of the complex **7** as a pale yellow solid.

Attempts to prepare complexes of binaphthalene thioethers **1** with a more demanding substituent on the sulfurs, such as isopropyl, have been so far unsuccessful since no reaction occurred at room temp.

Molecular Structure of [$PdCl_2(Me_2BINAS)$], (**6**): The molecular structure of **6** has been determined by X-ray diffraction analysis. A view of the molecule is given in Figure 2 and the most significant bond angles and lengths are listed in Table 1.

Figure 2. PLUTON[16] view of the molecular structure of $[PdCl_2(Me_2BINAS)]$ (**6**)

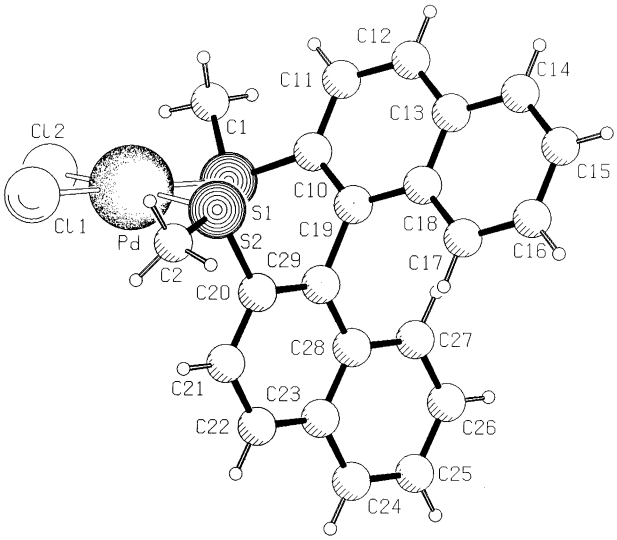


Table 1. Selected bond lenghts (Å) and angles (°) for complex $[PdCl_2(Me_2BINAS]$ (**6**)

Bonds (Å)		Angles (°)	
Pd-S1	2.316(2)	S1-Pd-S2	89.55(6)
Pd-S2	2.297(2)	Cl2-Pd-S2	175.73(6)
Pd-Cl1	2.285(2)	Cl2-Pd-S	187.57(6)
Pd-Cl2	2.305(2)	Cl1-Pd-S2	92.45(6)
C1-S1	1.805(9)	Cl1-Pd-S1	177.76(6)
S2-C2	1.791(7)	Cl1-Pd-Cl	290.38(7)
		Pd-S1-C1	107.29(26)
		Pd-S2-C2	112.19(25)

The crystal contains discrete mononuclear units of **6** in which the dithioether acts as a chelate ligand in a seven-membered ring with a highly distorted twisted chair conformation. Both the methyl groups are located in a pseudo-equatorial position giving the structure an overall C_2-symmetry, where the Pd atom is located on a two-fold axis. Both S-stereocenters display a pyramidal geometry and have the same relative configuration, whereas the binaphthyl moiety has the opposite chiral notation. As expected, the naphthyl rings are significantly bent and with a dihedral angle of 110.9(1)° between their planes, which allows the opposing hydrogens at C17 and C27 to be located at a comfortable distance apart (2.830(6) Å). These data suggest that the chiral diaryl backbone is, basically, free from torsional strain.

On the contrary, fairly short distances have been calculated between the hydrogen at C11 and two hydrogen atoms

of the C1-methyl (2.108(9) and 2.333(9) Å), and between the hydrogen at C21 and one hydrogen atom of the C2-methyl (2.189(9) Å). This may cause some destabilization of the diequatorial structure with respect to those structures with the methyl group(s) in an axial disposition.

The coordination around the Pd atom is essentially square planar. The Pd−S bond distances (2.297(2) and 2.316(2) Å) are comparable with those observed in other Pd complexes with diaryl[3] or aryl alkyl[4] sulfide ligands (2.293 and 2.288 Å, respectively). The Pd−Cl bond lengths (2.285(2) and 2.305(2) Å) are in the normal range for Pd chlorides with a *trans*-thioether donor[5], but are some seventy standard deviations shorter than those in *trans*-phosphane complexes (2.362 and 2.367 Å)[6]. This difference gives a measure of the weaker *trans* influence of the sulfur as compared to the phosphorus donor. The remaining bond distances and angles within the structure of the dithioether ligand are unexceptional.

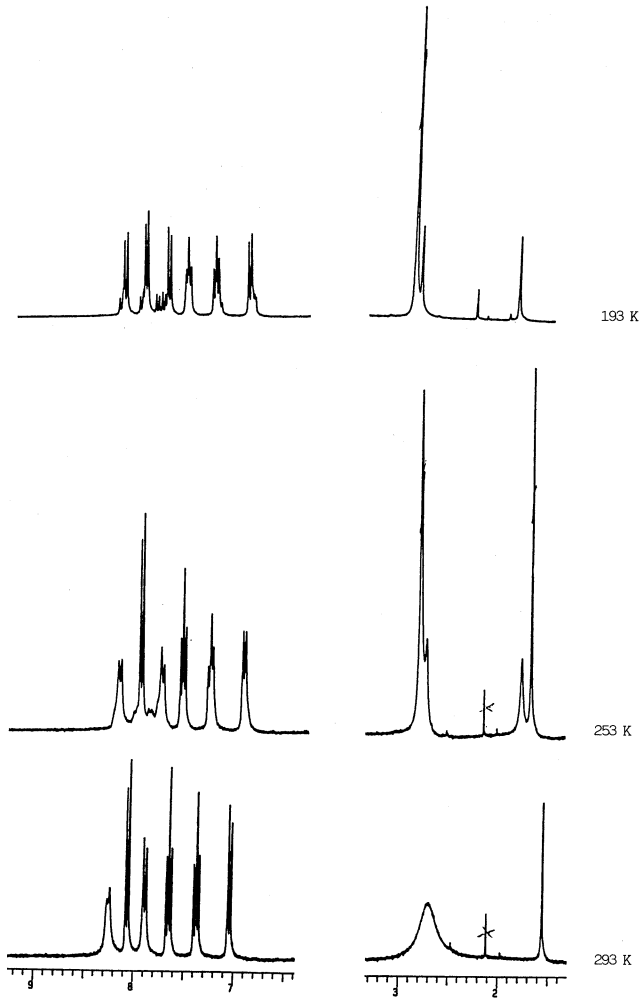
Of the possible stereoisomers of the complex **6**, which differ either in the conformation of the chelate ring or in the spatial arrangement of the *S*-methyl substituents, this one is expected to be the most stable because both methyl groups are located in equatorial positions of the energetically favoured twisted chair conformation[7]. Although its preferential separation in the crystalline form obtained from the solution does not necessarily depend on a higher inherent stability, but may only reflect small differences in solubility or in crystal packing energy, NMR evidence is in keeping with the view that this isomer corresponds to the main product present in solution at low temperature.

Variable-Temperature NMR Characterization: The proton NMR spectrum of the rhodium complex **5** (X = ClO_4) shows, in the non aromatic region, two multiplets (4 H) at δ = 4.76 and 4.36, two broad signals (2 H) at δ = 2.47 and 2.10 and a singlet (6 H) at δ = 2.42 for the *S*-methyl protons. The first four resonances can be attributed to the *exo*- and *endo*-olefinic protons and to the methylene groups of the coordinated cyclooctadiene, respectively. The aromatic part of the spectrum is characterized by the presence of six peaks in the range δ = 8.21−7.00, roughly four doublets (2 H) and two triplets (2 H), which corresponds to the typical pattern of a C_2-symmetrical 2,2′-disubstituted binaphthalene. The shape of the NMR spectrum is not affected when the sample is cooled down to 193 K. In particular, the methyl resonance at δ = 2.42 does not show any apparent splitting.

The variable-temperature proton NMR spectrum of the palladium complex **6** is shown in Figure 3. At room temp. **6** shows a C_2-symmetrical pattern for the aromatic protons of the binaphtalene backbone and a broad singlet at δ = 2.7 corresponding to both the *S*-methyl substituents.

A less significant, but not negligible line broadening is also apparent in two aromatic peaks in the low field region of the spectrum. At 253 K, the two aromatic and the *S*-methyl resonances resolve into two different signals in an approximate 4:1 ratio, and a new peak appears at about 1.7 ppm. From 233 K down to 193 K this last new signal is quite sharp and shows the same intensity as the lower intensity peak arising from the splitting of the original *S*-methyl resonance (Figure 3).

Figure 3. variable temperature ^{1}H-NMR spectrum of [$PdCl_2$(Me$_2$-BINAS)] (**6**)

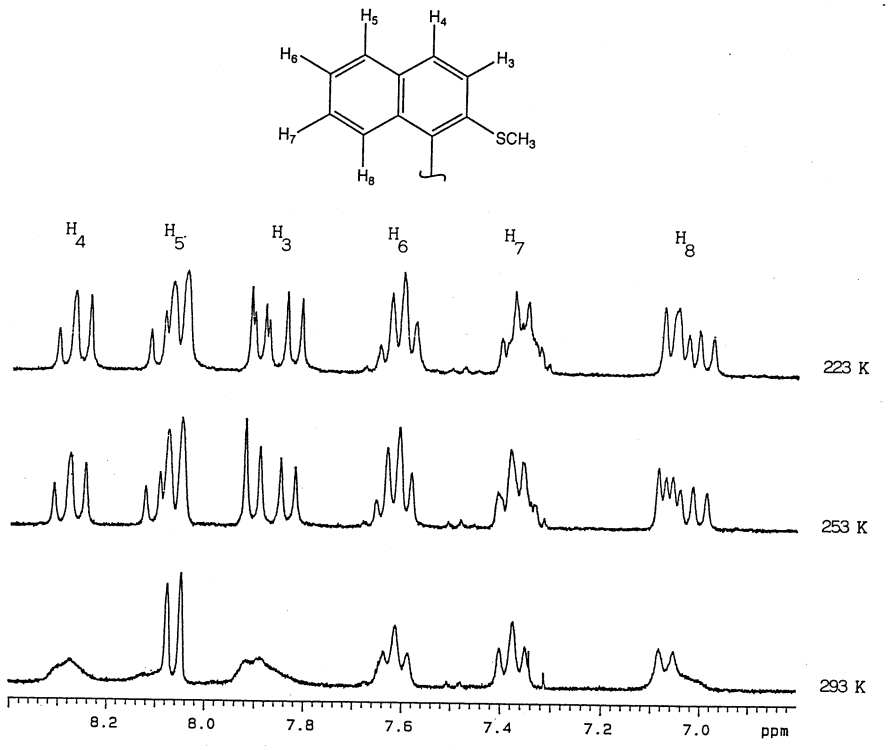


Since several stereoisomers with different spatial arrangements of the *S*-methyl substituents and different conformations of the seven-membered chelate ring are expected for the complex **6**, in principle this temperature dependent NMR spectrum may well reflect the presence of a dynamic equilibrium between two of these. An approximate energy barrier of 55 kJ mol^{-1} can be calculated for this process by line shape analysis of the variable temperature ^{1}H-NMR spectra, applying the coalescence temperature method[8].

The variable temperature ^{1}H-NMR spectra of the aromatic part of the platinum complex **7** is shown in Figure 4. The attributions to the protons have been assigned on the basis of selective decoupling and NOE experiments.

At room temp. the aromatic region shows six resonances with a pattern consistent with a C_2-symmetrical binaphthalene derivative. A significant line broadening is observed for the signals of three protons which apparently are close to the low exchange limit at room temp., while the remaining three protons give fairly sharp peaks. At 253 K all the aromatic protons give partially overlapping, sharp multiplets

Figure 4. Variable-temperature ^{1}H-NMR spectrum of [$PtCl_2(Me_2BINAS)$], (**7**): Aromatic part



indicative of the presence of a mixture of two C_2-symmetrical species in ratio of about 3:2. At a lower temperature the more abundant of these isomers undergoes a further dynamic process which leads to the formation of an additional product. Some resonances, in particular the one attributed to H_3, are further split into two separate sets of signals. The emerging stereoisomer at 223 K is apparently devoid of C_2-symmetry, as indicated by the number of observable peaks. Unfortunately, due to the poor solubility of the complex, the NMR spectra could not be recorded at temperatures lower than 223 K. These data show that at room temp. two diastereomeric platinum complexes are slowly interconverting and that the major one is involved in a further dynamic process at lower temperatures.

At room temp., the *S*-methyl groups give rise to three broad singlets at δ = 2.82, 2.72 and 1.80, of roughly the same intensity, which do not collapse even at 320 K. These peaks are all accompanied by Pt satellites, confirming the chelate coordination of the sulfur centers to the metal. At 253 K the approximate values of the $^3J_{Pt-H}$ of these couplings, from the most shielded to the most deshielded signal, are 38 Hz, 44 Hz and 41 Hz, respectively. These values are substantially constant in the range of temperature explored.

Correlated spectra indicate that the two resonances at higher field belong to the same product. This suggests that the predominant stereoisomer of **7** has two unequivalent methyl substituents resonating at δ = 2.72 and δ = 1.80, while the less abundant one has a C_2-symmetrical structure with two equivalent methyl groups resonating at δ = 2.82.

Irradiation of this peak causes a significant NOE enhancement of the H_3 proton on the naphthalene ring, which is consistent with an equatorial location for this methyl group. This indicates that the minor isomer has both methyl groups in equatorial position and the seven membered chelate ring in chair or twisted chair conformation, in order to fulfill the condition of C_2 symmetry.

When the methyl signal of the minor isomer at δ = 2.82 is under irradiation, it is apparent that also the resonances of the methyl groups of the major species at δ = 2.72 and 1.80 experience NOE and, vice versa, irradiation of these peaks shows a similar effect on the δ = 2.82 peak. These NOE experiments also indicate that the less shielded methyl resonance of the major isomer belongs to an equatorial methyl group, whereas the more shielded methyl resonance belongs to an axial group. From these data the major isomer of the platinum complex **7** can be assigned to having an ax-eq disposition of the methyl substituents.

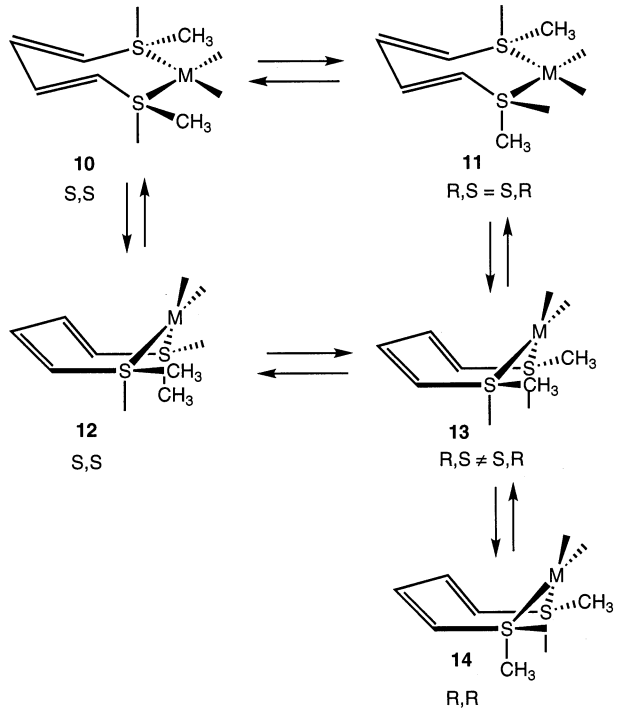
The peaks of the aromatic part of the NMR spectrum of the Pt complex are too close together and not appropriately shaped for a reliable determination of the activation energy of the dynamic processes to be achieved. However, the presence of well separated methyl resonances at room temp. indicates that this complex is less fluxional than the Pd counterpart and that the activation energy for the first equilibrium should be higher than the 55 kJ mol^{-1} found for the Pd complex.

Aside from the relative diastereomeric ratio and equilibration rates, the overall pictures emerging from the dynamic NMR investigation of the platinum and the palladium complexes are quite similar, with the basic difference that, unlike the platinum case, in the palladium complex it is the major species which has the eq−eq methyl groups.

Discussion

The dynamic behaviour shown by the Pd and Pt complexes indicates that different species are present in solution and that the interconversion among them is a fast process on the NMR timescale at room temp. Scheme 2 summarizes the interplay among the possible stereoisomers (diaxial species are omitted).

Scheme 2. Possible stereoisomers of Me_2BINAS complexes; the absolute configuration of the stereogenic sulfur centers are indicated; the binaphthalene backbone (R configuration) and the additional ligands at the metal are omitted for clarity



For the interconversion between these species three different hypothesis can be formulated: 1) interconversion between two different conformations of the seven membered chelate ring of comparable stability; 2) epimerization at the stereogenic sulfur through dissociation-recombination; 3) pyramidal inversion at the stereogenic sulfur in the bound state with no dissociation. In the first hypothesis the configurations at both the sulfur atoms are preserved during the dynamic process, while the second and the third transformations are accompanied by a net inversion of configuration at one or both stereogenic sulfur(s).

The fact that the position of the chemical shifts of the methyl substituents and the values of the relevant $^3J(^{195}Pt,^1H)$ coupling constants of the Pt complex are invariant in the temperature range scanned rules out the second hypothesis, and lends better support to the view that dissociation of the S donors is not occurring at any time.

From the NMR spectra of the platinum complex **7** two species can be univocally identified. The minor isomer has two equatorial *S*-methyl substituents and an overall C_2-symmetry. These conditions are met only by compound **10** having the seven membered chelate ring in a twisted chair (or chair) conformation, but not by the corresponding boat conformer **13**. The same chair structure can be attributed to the major isomer of the palladium complex which shows the same NMR pattern. Thus, the structure shown in the solid state by the Pd complex **6** corresponds to the structure of the predominant isomer in solution.

The second species identified by NMR has an equatorial-axial disposition of the methyl groups and is the predominant one in the Pt complex, even at room temp. Three different structures are conceivable for this isomer: one which mantains the twisted chair conformation and the C_2-symmetry (**11**) and two with a twisted boat conformation of comparable stability and C_1 symmetry (**12** and **14**). The ^{1}H-NMR spectra at −20°C suggest a C_2-symmetrical structure for this compound. While this condition is met by the chair conformer **11**, it cannot be overlooked that an apparent C_2 symmetry can result from a fast interconversion of two C_1-symmetrical stereoisomers such as **12** and **14**.

Actually, at −50°C a further dynamic process causes the C_2-symmetrical pattern of the aromatic resonances to be broken down. Notably, chemical shifts and shapes of the signals due to the methyl groups do not show any apparent change at this stage. As the surroundings of the methyl substituents are quite similar in **12** and **14**, both these facts seem to us to lend better support to the second assumption.

We can confidently conclude that in the case of the platinum complex **7**, the eq-eq chair conformer **10** is slowly interconverted at room temp. into the ax-eq boat conformers **12** and **14** which, under the same conditions, are rapidly interconverting. The same is probably true for the palladium derivative **6**, which is more fluxional than the Pt counterpart.

For the equilibration between **10** and **12** (or **14**) to occur, both changes in the chelate ring conformation and inversion of configuration at one stereogenic sulfur are required. The available data do not allow us to envisage which process is occurring first, but it is known that they are both feasible and can even take place simultaneously[9].

The structures having both the methyl groups equatorial are expected to be more stable, but this is not the case for the platinum complex where the predominant species has an axial methyl substituent. Actually, a non-bonding interaction is present between the hydrogen at the aryl carbon 3 (adjacent to that bound to the sulfur) and the equatorial methyl substituent. This is evidenced by a short contact distance in the solid state structure of the Pd complex (ca. 2.1 Å) and should be even more severe in the case of the Pt derivative due to the larger ionic radius. In keeping with this, the equilibrium of the platinum complex is shifted towards the ax-eq isomer.

Nothing can be said about the dynamics of the rhodium complex **5** which is probably highly fluxional over the range of temperatures scanned.

Conclusions

The dithioether complexes reported here are all fluxional at room temp. This dynamic behaviour is extremely pronounced in the case of rhodium(I) derivatives whose dia-

stereoisomers did not show isolated NMR resonances even at −80°C. Due to this property, Rh complexes with Me_2BINAS do not seem well suited for use in enantioselective catalysis where high e.e.'s should not be expected.

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Experimental Section

Melting points are uncorrected. Infrared spectra were recorded in KBr pellets on a BIO-RAD FTS-7PC spectrophotometer. ^{1}H and ^{13}C spectra were recorded on a Varian VXL 5000 spectrometer at 300 and 75.5 MHz, respectively, in CD_2Cl_2 and $CDCl_3$. Chemical shifts of protons and carbons are reported in ppm referred to TMS as an internal standard. Elemental analyses were performed with a Perkin Elmer Analyser 240 B. Commercial chemical reagents were used as received and solvents were dried by standard procedures and stored over molecular sieves under an inert atmosphere. $[Rh(cod)_2]^+X^-$[10], $PtCl_2(PhCN)_2$[11] and $PtCl_2(PhCN)_2$[12] were prepared according to the literature.

Preparation of [Rh(cod)(Me$_2$BINAS)]ClO$_4$ (**5**): The ligand Me_2BINAS (99.3 mg, 0.29 mmol) was added to a solution of $[Rh(cod)_2]ClO_4$ (100 mg, 0.24 mmol) in dichloromethane (5 ml). After stirring at room temp. for 15 min, diethyl ether was added to give a yellow precipitate of $[Rh(cod)(Me_2binas)]ClO_4$ which was filtered off and dried in vacuo (147.8 mg, 94% yield). − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1096 s, 625 m. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 9 Hz, 2 H, ArH); 8.04 (d, *J* = 8.2 Hz, 2 H, ArH); 7.76 (d, *J* = 8.5 Hz, 2 H, ArH); 7.58 (t, *J* = 7.6 Hz, 2 H, ArH); 7.34 (t, *J* = 8.2 Hz, 2 H, ArH); 7.00 (d, *J* = 9 Hz, 2 H, ArH); 4.76 (br. m, 4 H, CH cod); 4.36 (br. m, 4 H CH, cod); 2.42 (s, 3 H, CH_3); 2.10 (d, *J* = 9.3 Hz, 4 H, CH_2 cod); 1.80 (br. m, 4 H, CH_2 cod). No splitting is observed at low temperatures. − ^{13}C NMR ($CDCl_3$): δ = 133.9, 132.6, 130.2, 129.7, 129.1, 127.0, 124.6 (Ar); 82.0 (CH cod); 79.9 (CH, cod); 34.2 (CH_2, cod); 15.9 (SCH_3). − $RhC_{30}H_{30}S_2ClO_4$ (657.0): calcd. C 54.9, H 4.5, S, 9.7; found C 55.0, H 4.5, S 9.7.

Preparation of [PdCl$_2$(Me$_2$BINAS)] (**6**): The ligand Me_2BINAS (50 mg, 0.144 mmol) was added to a solution of $[PdCl_2(PhCN)_2]$ (50 mg, 0.13 mmol) in dichloromethane (5 ml). After stirring at room temp. for 20 min, diethyl ether was added to give a red precipitate of **6** which was filtered off and dried in vacuo (54.1 mg, 73.1% yield). − ^{1}H NMR ($CDCl_3$): see text. − Mass spectrum (FAB); *m/z*: 523 (M^+), 489 (M − Cl), 452 (M − 2 Cl), 346 (Me_2binas). − Conductivity in CH_2Cl_2: 0.041 S·cm^2·eq^{-1}. − $C_{22}H_{18}Cl_2PdS_2$ (523.8): calcd. C 50.4, H 3.4, S 12.2; found C 50.6, H 3.3, S 12.1.

Preparation of [PtCl$_2$(Me$_2$BINAS)] (**7**): The ligand Me_2BINAS (172 mg, 0.5 mmol) was added to a solution of $[PtCl_2(PhCN)_2]$ (235 mg, 0.5 mmol) in chloroform (45 ml) and the solution was irradiated (254 nm) at 35°C for 11 h. The chloroform was evaporated and the yellow residue was taken up with benzene (20 ml). The yellow precipitate was filtered off and dried in vacuo (160 mg, 53% yield). − ^{1}H NMR ($CDCl_3$): see text. − $C_{22}H_{18}Cl_2PtS_2$ (612.5): calcd. C 43.11, H 2.96; found C 43.11, H 2.96.

X-ray Structure Determination and Refinement of [PdCl$_2$(Me$_2$BINAS)] (**6**): X-ray quality crystals of the complex **6** were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution. $C_{22}H_{18}ClPd_2S_2$, *M* = 523.81. Monoclinic, *a* = 8.144(2), *b* = 27.416(7), *c* = 9.416(2), β = 92.98(2), V = 2099(1) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflexions, λ = 0.71069 Å), space group $P2_1/c$ (No. 14), *Z* = 4, D_x = 1.657 g cm^{-3}. Yellow, air stable crystals, μ(Mo-K_α) = 13.42 cm^{-1}. CAD4 diffractometer, ω/2θ mode with ω scan width = 0.80 + 0.35 tan θ, ω scan speed 1.3−5.5° min^{-1}, graphite-monochromated Mo-K_α radiation. Reflection ranges for the data collection were 1° < θ < 25° and −9 ≤ *h* ≤ 9, 0 ≤ *k* ≤ 32, 0 ≤ *l* ≤ 11. 3690 unique reflections (Lp and empirical absorption correction from ψ scans[13], minimum/maximum transmission = 0.786:0.999), 2634 observed reflections with $I > 2\sigma(I)$. Direct methods (SHELXS-86 program)[14] and full-matrix least-squares refinement on F^2 for all the reflections (SHELXL-93 program)[15] were applied.

Naphthyl groups were refined as rigid groups because some of their geometrical parameters were not sensible, and at the end of refinement were close to standard values. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions with isotropic temperature factors fixed at 1.2 times (naphthyl H) or 1.5 times (methyl H) U_{eq} for the corresponding carbon atoms. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.1075P)^2]$ where $P = [\max(F_o^2,0) + 2F_c^2)]/3$. Final R(*F*) and $R_w(F^2)$ values were 0.047 and 0.148 for reflections with $I > 2\sigma(I)$. Thermal parameters, a complete list of bond lengths and angles and further details of **6** are available from Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quotation of the depository number CSD-407608.

[1] [1a] C. Claver, S. Castillon, N. Ruiz, G. Delogu, D. Fabbri, S. Gladiali, *Chem. Commun.* **1993**, 1833. − [1b] N. Ruiz, A. Aaliti, J. Fornies, A. Ruiz, C. Claver, C. J. Cardin, D. Fabbri, S. Gladiali, *J. Organomet. Chem.*, in press.
[2] Review: S. Gladiali, J. C. Bayón, C. Claver, *Tetrahedron Asymmetry* **1995**, *6*, 1453.
[3] L. R. Gray, D. J. Gulliver, W. Levason, M. Webster, *Acta Crystallogr. C* **1983**, *39*, 877.
[4] G. R. Clark, J. D. Orbell, *J. Organomet. Chem.* **1981**, *215*, 121.
[5] B. de Groot, G. S. Hanan, S. J. Loeb, *Inorg. Chem.* **1991**, *30*, 4644.
[6] [6a] D. S. Payne, J. A. A. Mukuolu, J. C. Speakman, *Chem. Commun.* **1965,** 599; − [6b] R. A. Jacobson, L. L. Martin, *Inorg. Chem.* **1971**, *10*, 1795.
[7] D. F. Bocian, H. L. Strauss, *J. Am. Chem. Soc.* **1977**, *99*, 2876.
[8] A. A. Watson, A. C. Willis, S. B. Wild, *J. Organomet. Chem.* **1993**, *445,* 71.
[9] A. Albinati, J. Eckert, P. Pregosin, H. Rüegger, R. Salzman, C. Stössel, *Organometallics* **1997**, *16*, 579.
[10] R. Usòn, L. A. Oro, M. A. Garralda, C. Claver, P. Lahuerta, *Transition Met. Chem.* **1979**, *9*, 55.
[11] M. S. Karasch, R. C. Seyler, F. R. Mayo, *J. Am. Chem. Soc.* **1938**, *60*, 882.
[12] F.R. Hartley, *Organomet. Chem. Rev. A* **1970**, *6*, 119.
[13] A. C. T. North, P. C. Philips and F. S. Mathews, *Acta Crystallogr., Sect. A* **1968**, *24*, 351.
[14] G. M. Sheldrick, SHELXS 86, in *Crystallographic Computing 3* (Eds.: G. M. Sheldrick, C. Krüger, R. Goddard), Oxford University Press, Oxford, **1985**, pp. 175−178.
[15] G. M. Sheldrick, *SHELXL 93, A Program for the Refinement of Crystal Structures,* University of Göttingen, Göttingen, **1992**.
[16] A. L. Spek, *PLUTON 93, A Program for the Display and Analysis of Crystal and Molecular Structures,* University of Utrecht, The Netherlands, **1993**.

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