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The synthesis and stereodynamics of platinum(II) chloride complexes of 1,1′-bis(methylthio)ferrocene, 1,1′-bis(methylseleno)ferrocene and 1,1′-bis(methylthio)ruthenocene

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Abstract

The complexes $[PtCl_2(L–L)]$ (L–L = $[(C_5H_4SCH_3)_2Fe]$, $[(C_5H_4SeCH_3)_2Fe]$, $[(C_5H_4SCH_3)_2Ru]$) have been synthesised. A ^1H NMR study of their solution properties showed that at high temperatures pyramidal inversion of the chalcogen atoms is rapid on the NMR timescale. At low temperatures (ca. −10 °C) the motion was arrested and the selenium complex existed as a mixture of *meso* and DL species in approximately equal proportions, whereas the sulphur complexes were predominantly (> 85%) in the DL form. Variable temperature bandshape analyses of the complexes yielded sulphur inversion (DL → DL) values of ΔG^* (298 K) of 64.18 ± 0.03 and 66.29 ± 0.09 kJ mol^{-1} for the iron and ruthenium compounds respectively and a selenium inversion (*meso* → DL) value of ΔG^* (298 K) of 78.8 ± 0.6 kJ mol^{-1}.

Introduction

The observation of chalcogen inversion in transition metal complexes was first reported in 1966 and involved the platinum(II) complexes $[PtCl_2(MeSCH_2CH_2SMe)]$ [1] and *cis*-$[PtCl_2(R_2S)_2]$ (R = $PhCH_2$, Et) [2]. These initial reports led to a wide-ranging investigation of pyramidal chalcogen inversion by detailed dynamic NMR studies, from which a number of novel intramolecular motions of chalcogen-containing ligands have been identified [3].

Some studies involving Pd(II) and Pt(II) complexes containing the organometallic ligands $[Fe(C_5H_4SR)_2]$ (R = Me, Ph, i-Pr, i-Bu) have been reported [4], but a detailed study of the complexes where R = Me was precluded by the insolubility of the materials. This paper describes the preparation, spectroscopic properties and chalcogen inversion energies of the compounds *cis*-$[PtCl_2(L–L)]$ (L–L = 1,1′-bis(methylthio)ferrocene, (BMSF), 1,1′-bis(methylseleno)ferrocene, (BMSEF), 1,1′-bis(methylthio)ruthenocene, (BMSR)). The aim of the work was to prepare and

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study complexes in which the $PtCl_2$ moiety was always present, so that direct comparisons could be made between the influences of the ligands on the properties of the complexes.

Experimental

General

All preparations were carried out by standard Schlenk techniques [5]. All solvents were freshly distilled, dried and degassed before use, and all reactions were performed under purified nitrogen.

The following materials were prepared by published methods: $[PtCl_2(NCPh)_2]$ [6], 1,1′-bis(methylthio)ferrocene (BMSF) [7], 1,1′-bis(methylseleno)ferrocene (BMSEF) [7], and 1,1′-bis(methylthio)ruthenocene (BMSR) [8].

Elemental analyses were carried out by Butterworth Laboratories Ltd., Teddington, Middlesex, London and by C.H.N. Analysis, South Wigston, Leicester.

^1H NMR spectra were recorded on a Bruker AM250 spectrometer, operated at 250.13 MHz. All spectra were recorded with $CDCl_2 \cdot CDCl_2$ solutions with Me_4Si as internal standard. A standard B-VT1000 variable temperature unit was used to control the probe temperature, the calibration of this unit being checked periodically against a Comark digital thermometer. The temperatures are considered to be accurate to $\pm 1°C$. Bandshape analyses were performed by use of modified versions of the program DNMR3 devised by Kleier and Binsch [9,10].

Synthesis of the complexes

All the complexes were prepared similarly, the only variable being the time of reaction. Details of the synthetic and analytical data are given in Table 1, and a representative preparation is outlined below.

$[PtCl_2(NCPh)_2]$ (0.236 g, 0.5 mmol) was dissolved in benzene (40 cm^3) with a little gentle warming. A solution of BMSR (0.20 g, 0.62 mmol) in benzene (20 cm^3) was added and the mixture stirred for 16 hours. The yellow precipitate formed was filtered off, washed with hexane (2×20 cm^3) then benzene (2×20 cm^3), and dried *in vacuo* to give $[PtCl_2(BMSR)]$. Yield 0.146 g (50%).

Results and discussion

The ligands BMSF, BMSEF and BMSR react smoothly with $[PtCl_2(NCPh)_2]$ to give good yields of the complexes $[PtCl_2(BMSF)]$, $[PtCl_2(BMSEF)]$ and

Table 1

Synthesis and characterisation of the complexes *cis*-$[PtCl_2(L\text{-}L)]$

Complex	Reaction time (h)	Yield [a] (%)	Melting temperature [b] (°C)	Analytical data			
				Found (%)		Calculated (%)	
				C	H	C	H
$[PtCl_2(BMSF)]$	0.5	65	240–250	26.6	2.7	26.5	2.6
$[PtCl_2(BMSEF)]$	1	59	220–240	23.1	2.3	22.6	2.2
$[PtCl_2(BMSR)]$	16	50	250–270	24.7	2.4	24.5	2.4

[a] = Yields quoted relative to $[PtCl_2(NCPh)_2]$. [b] Decomposition.

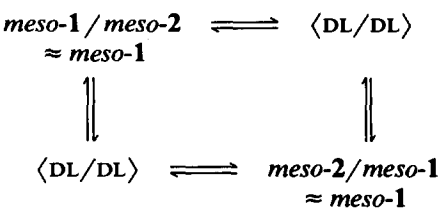
[$PtCl_2$(BMSR)], respectively. All the products are yellow, air-stable solids, which are only sparingly soluble in organic solvents.

NMR Spectroscopy

Although the poor solubility of the complexes caused difficulties, low temperature ^{1}H NMR spectra were obtained in each case (Fig. 1). The spectral data are listed in Table 2.

From the cyclopentadienyl ring proton and the chalcogen-methyl regions of the spectra it was evident for all the complexes that more than one species was present in solution at low temperatures. By use of the arguments, mainly based on steric grounds, which were developed in earlier studies [4], detailed assignments were made as indicated in Table 2.

When the temperature of each NMR sample was raised, exchange broadening occurred, until at high temperature for each complex two averaged signals in the ring-proton region and one chalcogen-methyl signal with Pt satellites were observed. As discussed in previous papers [7,8], complexes involving these ligands have the potential to undergo both chalcogen inversion and bridge reversal. If either or both of these processes are slow on the NMR timescale then four configurational isomers can exist, namely *meso*-**1**, *meso*-**2**, and a degenerate DL pair. These species can be related by the corners of a cube, Fig. 2. It has been argued in earlier work [4] that, at the temperatures under consideration, bridge reversal is rapid and therefore the NMR spectral changes are due solely to chalcogen inversion which interchanges bridge reversal-averaged DL and *meso* species. In each complex the degenerate DL pairs will thus appear as averaged pseudo-planar –E–Pt–E– bridge structures. Also the *meso*-**1**/*meso*-**2** averaging will strongly favour the *meso*-**1** structure because of the steric crowding of the E-methyls in the *meso*-**2** species. Thus the graph diagram can be simplified to:



The relative populations of the invertomers varies amongst the complexes and although the DL is invariably dominant, it constitutes only a slight excess in [$PtCl_2$(BMSEF)]. In this case the large selenium atoms probably cause a steric interaction between a chlorine and a methyl group in the DL form and thus favour a greater population of *meso*-**1** invertomer.

Dynamic NMR studies

Bandshape analysis was undertaken for the three complexes but differing approaches were necessary. Due to the low intensity of the *meso*-**1** signals in [$PtCl_2$(BMSF)] and [$PtCl_2$(BMSR)], bandshape analysis was restricted to the ring-methine signals of the DL invertomers. The spin problem involves interconversion between a degenerate pair of pseudo-planar DL conformers the exchange being of

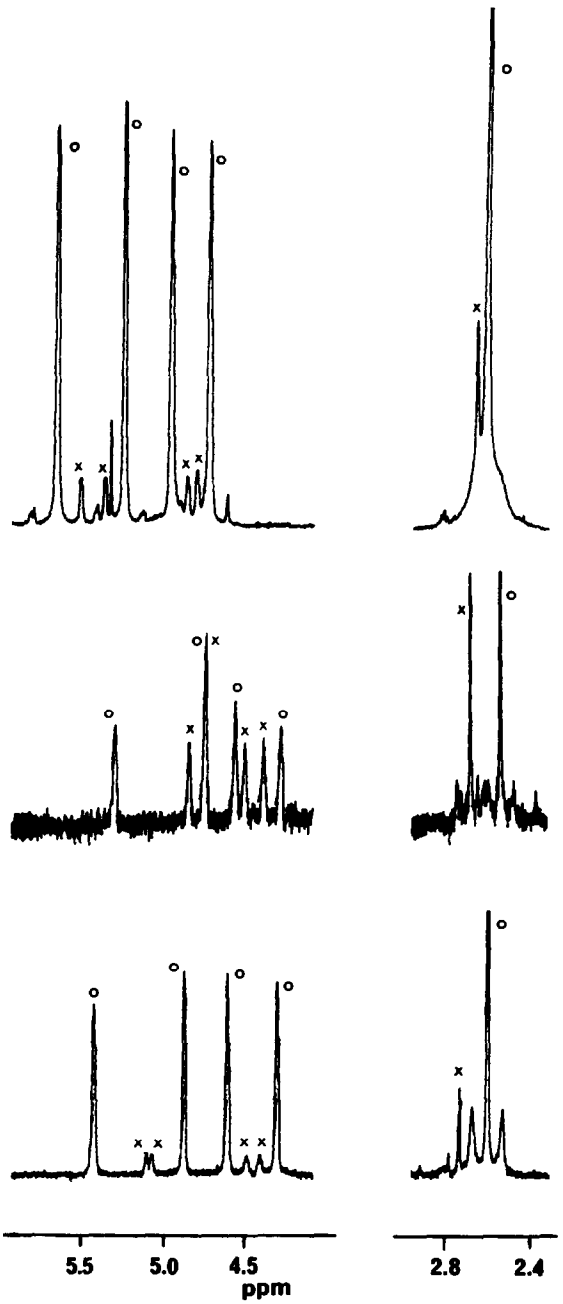


Fig. 1. Low temperature ^1H NMR spectra (−10 °C) of $[PtCl_2(BMSR)]$ (top), $[PtCl_2(BMSEF)]$ (middle), $[PtCl_2(BMSF)]$ (bottom). × = *meso*-**1**, ○ = DL.

the type ABCD ⇌ BADC, in the absence of inter-ring coupling, Fig. 3. The labelling of the four signals was undertaken on the basis of a high frequency shift imposed on the ring protons by the E-Me group, with H_A and H_B being more affected than H_C

Table 2

^{1}H NMR parameters for the complexes [$PtCl_2$(L–L)] in $C_2D_2Cl_4$ at high and low temperatures

Complex	Temperature (°C)	Solution species	Invertomer population (%)	Chemical shift E-Me protons (δ)	Chemical shift ring protons (δ) [a]	
[$PtCl_2$(BMSF)]	−10	DL	88	2.60(t) (46.0) [b]	5.42	4.86
					4.60	4.29
		meso-**1**	12	2.77 [c]	5.09	5.06
					4.48	4.40
	60	*meso*/DL	100	2.65(t) (46.1) [b]	5.13	4.42
[$PtCl_2$(BMSEF)]	−10	DL	54	2.50(t) (39.0) [b]	5.30	4.75
					4.56	4.28
		meso-**1**	46	2.68(t) (40.0) [b]	4.84	4.75
					4.50	4.38
	130	*meso*/DL	100	2.68(t) (36.0) [b]	4.84	4.49
[$PtCl_2$(BMSR)]	−10	DL	85	2.58(t) (45.0) [b]	5.63	5.22
					4.92	4.68
		meso-**1**	15	2.64 [c]	5.48	5.34
					4.82	4.76
	80	*meso*/DL	100	2.68(t) (46.0) [b]	5.51	4.88

[a] Signals show weak multiplet structure in most cases. [b] ^3J(PtH)/Hz values. [c] ^{195}Pt satellites obscured due to overlapping signals and low intensity.

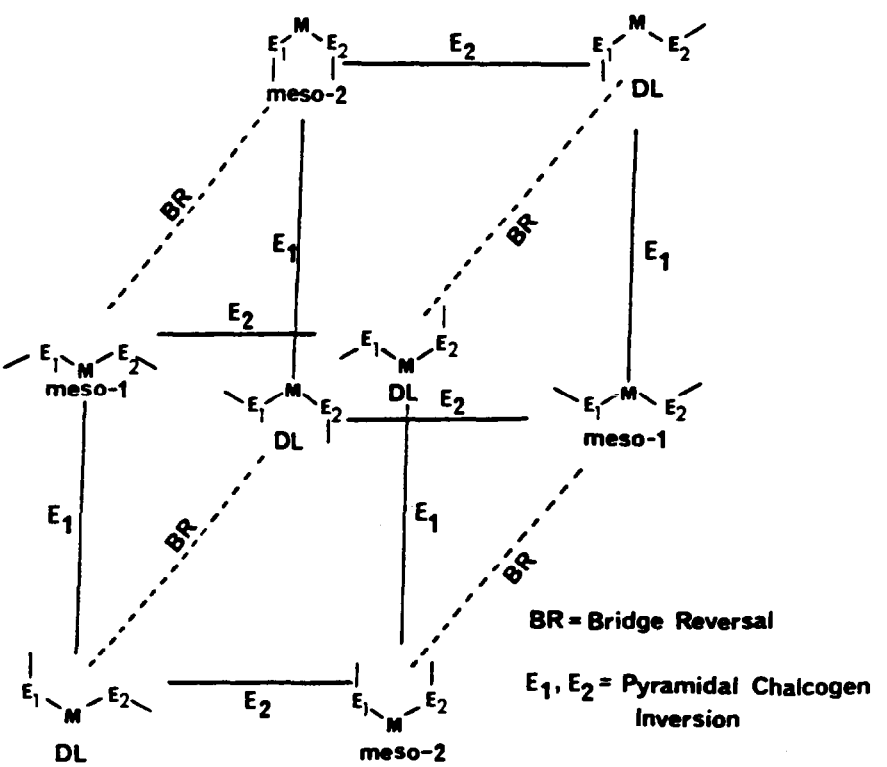


Fig. 2. Diagram showing the relationships of the static invertomer species of [$PtCl_2$(L–L)] (L–L = BMSF, BMSEF, BMSR).

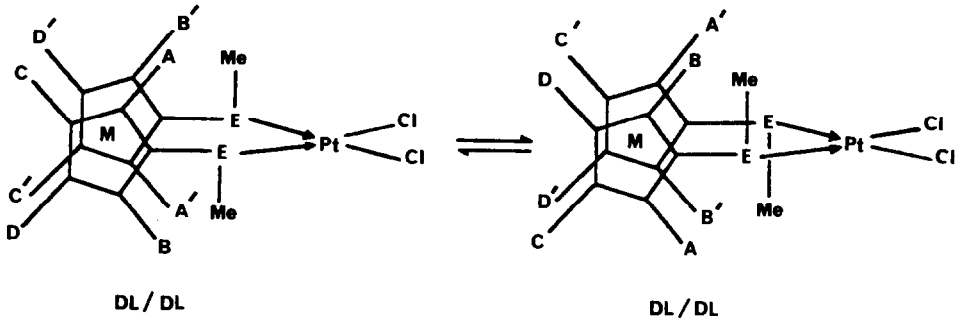


Fig. 3. The bridge reversal-averaged invertomers of $[PtCl_2(BMSF)]$ and $[PtCl_2(BMSR)]$ showing the methine proton labelling.

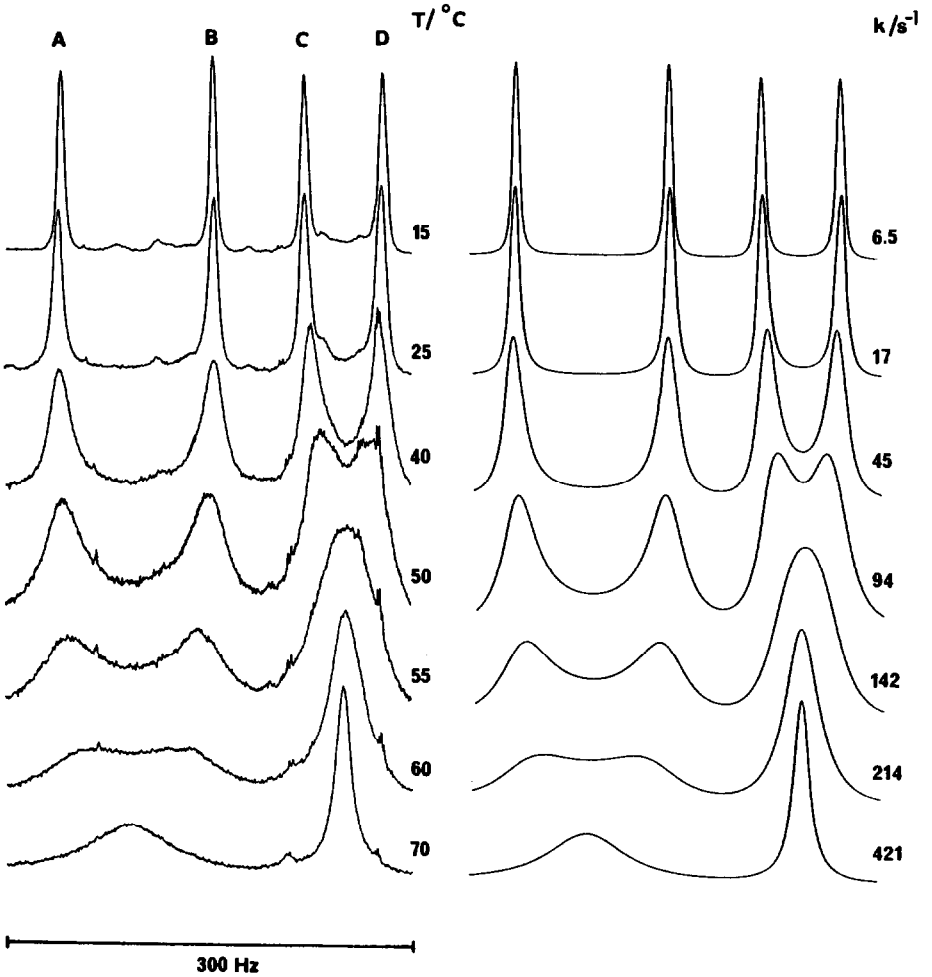


Fig. 4. The experimental (left) and computer synthesised ^1H NMR spectra (methine region) of $[PtCl_2(BMSR)]$ showing the 'best-fit' rate constants for each temperature.

Table 3

Arrhenius and Eyring activation parameters for chalcogen inversion in the complexes $[PtCl_2(L-L)]$

Complex	E_a (kJ mol^{-1})	$\log_{10}A$	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$\Delta G^{\neq}$ (298 K) (kJ mol^{-1})
$[PtCl_2(BMSF)]$ [a]	76.2±0.6	14.9±0.1	73.6±0.6	31.7±2.0	64.18±0.03
$[PtCl_2(BMSEF)]$ [b]	83.0±3.2	13.5±0.5	79.9±3.2	3.8±8.8	78.8 ±0.6
$[PtCl_2(BMSR)]$ [a]	61.1±1.6	11.9±0.3	58.5±1.5	−26.0±4.8	66.29±0.09

[a] ⟨DL⟩ → ⟨DL⟩ [b] ⟨*meso*⟩ → ⟨DL⟩

and H_D. The distinction between H_A and H_B and between H_C and H_D was less certain but was not essential for bandshape fitting. Simulations were carried out using ^3J(HH) and ^4J(HH) values from earlier studies [11] on ferrocenophanes and excellent fits were obtained between experimental and computed spectra (Fig. 4).

The ring-proton signals of the DL and *meso* invertomers of $[PtCl_2(BMSEF)]$ were insufficiently differentiated for accurate DNMR analysis and although 2D-EXSY studies [12,13] may have aided this problem, this approach was precluded by the insolubility of the material. Therefore $[PtCl_2(BMSEF)]$ was analysed using the Se-Me region of the spectrum and the *meso*-DL exchange was investigated as a simple two-site proton exchange problem with platinum satellites.

The activation parameters for the complexes are listed in Table 3. Although the *meso* species were neglected in the analysis of $[PtCl_2(BMSF)]$ and $[PtCl_2(BMSR)]$, it is reasonable to compare the resulting energy barriers to chalcogen inversion for all three complexes. The difference in ground state energies of DL and *meso*-**1** species does affect the $\Delta G^{\neq}$ values but, because of the similar populations of the invertomers in $[PtCl_2(BMSEF)]$, only by 0.4 kJ mol^{-1}, and hence a direct comparison of the energy barriers is valid.

The $\Delta G^{\neq}$ values are within the range found for chalcogen-containing Pt(II) complexes [4,14] but are noticeably greater than those found for other metal complexes containing these organometallic ligands [7,8,15,16], and in particular show at least a 20 kJ mol^{-1} increase over the values for $PtXMe_3$ complexes. The influence of the S-substituent on the sulphur inversion energy may be seen by comparing the $\Delta G^{\neq}$ value of 64.2 kJ mol^{-1} for S-Me inversion in the present complex $[PtCl_2(BMSF)]$ with the values of 65.0 and 66.7 kJ mol^{-1} for S-i-Bu and S-i-Pr inversions respectively in the complexes $[PtCl_2(C_5H_4SR)_2Fe]$ (R = i-Bu, i-Pr) studied previously [4]. The energy order is clearly a consequence of both electronic and steric effects. The $\log_{10}A$ and $\Delta S^{\neq}$ values for the present complexes are not as positive as those determined for other complexes in this series [7,8,15,16]. In previous papers involving complexes of these ligands we have suggested that the flexibility, as represented particularly by the rapid bridge-reversal process plays a part in determining the magnitude of these parameters. For the Pt(II) complexes a rationale may be that the strong Pt–E bonds and higher torsional barriers will produce a slower bridge reversal and thereby reduce the overall flexibility of the system.

In conclusion, this study has demonstrated that the $\Delta G^{\neq}$ parameter for chalcogen inversion changes in the expected manner, namely that for S inversion is lower than that for Se inversion, and also that the parameter is virtually unaffected by a change in the metallocene ligand backbone. In solution the most abundant in-

vertomer is invariably the DL species, but the relative populations of invertomers are dependent on the chalcogen present and to a much lesser extent on the metallocenyl backbone.

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