ATOMIC INVERSION BARRIERS OF SULPHUR AND SELENIUM IN THE DIMETHYLSULPHIDE AND DIMETHYLSELENIDE COMPLEXES OF THE HALOGENO CARBONYLS OF RHENIUM

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Summary

We have synthesised four rhenium carbonyl complexes of general formula $[ReX(CO)_3(Me_2E)_2]$ (X = Cl, Br, I, E = S, Se), and studied their temperature variable NMR spectra. All complexes were formed as the *fac* isomer, with the exception of $[ReI(CO)_3(Me_2Se)_2]$, which was obtained as a mixture of *mer* and *fac* forms. In all of these *fac* complexes pyramidal inversion of sulphur or selenium atoms has been demonstrated, and energy barriers to inversion have been determined either by computer simulation of complete line shapes or by coalescence temperature methods. The value of $\Delta G^{\ddagger}$ for inversion in this class of complex has been found to be about 17 kJ mol^{-1} higher for selenium than for sulphur, and variation of the *cis* halogen made no pronounced effect.

Introduction

Several di-substituted rhenium(I) carbonyl halide complexes in *fac* form have been reported with dialkyl- and diaryl-sulphides, -selenides and -tellurides [1]. However, *mer* isomers of the di-substituted rhenium(I) carbonyl halides have also been reported with other ligands [2,3].

Since the original observations of tetrahedral atomic inversion in coordination complexes of organic sulphides [4,5] there have been several studies of the phenomenon and the associated thermodynamic parameters [6—10]. These have usually involved the observation by DNMR of either prochiral methylene groups [5—7] or isomer mixtures in chelate complexes [10—11]. Only in certain special cases of molecular symmetry can two methyl groups on the same ligand atom be anisochronous. Thus for example in *mer*-[IrCl$_3$(CO)(PhMe$_2$P)$_2$] the two methyls on each individual phosphorus cannot be differentiated, but in the corresponding complex *fac*-[IrCl$_3$(CO)(PhMe$_2$P)$_2$] the removal of one plane of symmetry renders the two methyl groups on an individual phosphorus anisochronous, and observable as separate proton resonances [12]. This latter condi-

tion also applies in the complexes *fac*-[PtXMe$_3$(Me$_2$E)$_2$] (X = Cl, Br, I, E = S and Se), provided the atomic inversion about sulphur and selenium is arrested at low temperature [13]. The onset of ligand atom inversion causes the methyl groups on each sulphur or selenium to become isochronous, and thermodynamic parameters for the processes to be obtained. The rhenium(I) complexes *fac*-[ReX(CO)$_3$(Me$_2$E)$_2$] are both isoelectronic and isostructural with the platinum(IV) complexes *fac*-[PtXMe$_3$(Me$_2$E)$_2$], and therefore possess the same advantages in symmetry for the study of atomic inversion at sulphur and selenium in the absence of a prochiral organic group.

Results and discussion

Four complexes of the general formula [ReX(CO)$_3$(Me$_2$E)$_2$] have been synthesized by the direct action of dimethylsulphide or dimethylselenide upon the appropriate halogenopentacarbonylrhenium(I). The three possible structures for these complexes are illustrated in Fig. 1.

In the cases of [ReCl(CO)$_3$(Me$_2$S)$_2$], [ReCl(CO)$_3$(Me$_2$Se)$_2$] and [ReBr(CO)$_3$-(Me$_2$Se)$_2$] there were three strong infrared CO stretching modes of approximately equal intensity (Table 1), suggesting strongly the *fac* structure which would have such a pattern (A' (1) + A' (2) + A'') of bands. This was confirmed by the NMR spectra (vide infra). In the complex [ReI(CO)$_3$(Me$_2$Se)$_2$], however, a well resolved spectrum showed the presence of five bands in the CO stretching region, indicating a mixture of isomers. From previous arguments [3] this is likely to be the *mer*-1 isomer, which would also have three (A_1 (1) + A_1 (2) + B_1) infrared-active CO stretching modes. The presence of five instead of six bands is likely to be the result of a fortuitous overlap of the bands in different isomers. The identification of the minority extra isomer as *mer*-1 is further confirmed by NMR spectra (vide infra).

Even allowing rapid rotation about the Re ← E bonds in these complexes, the absence of pyramidal atomic inversion about the ligand atoms renders the methyl groups on each ligand anisochronous (see Fig. 2.). This can only be the case for the *fac* isomer, as a result of the absence of any symmetry plane through either of the Re ← E bonds. The onset of atomic inversion about E would, however, provide a pathway for the equalization of Me^A and Me^B.

The ^{1}H NMR spectrum of [ReCl(CO)$_3$(Me$_2$S)$_2$] consists of a well resolved doublet at ~−70°C (Table 2), which collapses (reversibly) to a sharp singlet on
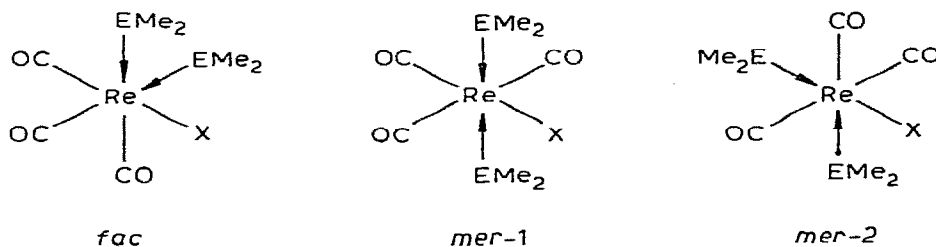

Fig. 1. The three possible structures for the complexes [ReX(CO)$_3$(Me$_2$E)$_2$].

SYNTHESIS AND CHARACTERIZATION OF THE COMPLEXES [ReX(CO)$_3$(Me$_2$E)$_2$]

Complex	Colour	m.p. (°C)	Yield (%)	Analysis: Found (Calc.)(%)		v(CO) (cm^{-1})
				C	H	
[ReCl(CO)$_3$(Me$_2$S)$_2$]	White	83— 86	73	19.3 (19.5)	2.68 (2.81)	2016, 1938, 1906 [a]
[ReCl(CO)$_3$(Me$_2$Se)$_2$]	White	97	70	16.0 (16.1)	2.27 (2.30)	2030, 1934, 1902 [a]
[ReBr(CO)$_3$(Me$_2$Se)$_2$]	White	101	71	14.8 (14.8)	2.27 (2.12)	2034, 1938, 1904 [a]
[ReI(CO)$_3$(Me$_2$Se)$_2$]	Pale Yellow	100—102	75	13.6 (13.7)	1.86 (1.96)	2054, 2036, 1944, 1926, 1910 [b]

[a] In chloroform, there were no indications of extra peaks. [b] In heptane, there were unresolved peaks in the chloroform solution spectrum, which were easily distinguished in the heptane spectrum.

temperature increase. The separate ^{1}H resonance of added dimethylsulphide does not exchange with the signals due to coordinated ligand at any temperature up to ca. 80°C above the AB coalescence temperature. The characteristics of these spectra confirm the *fac* form of this complex, and $\Delta G^{\ddagger}$ for the inversion barrier at sulphur was obtained from the coalescence temperature.

In the case of [ReCl(CO)$_3$(Me$_2$Se)$_2$] there was insufficient difference in the chemical shifts of the protons in the diastereotopic methyl groups to allow observation of the arrest of selenium inversion. The presence of two distinct ^{13}C signals for the methyl groups at —13°C, and their coalescence at higher temperature, could, however, be utilized to study the ligand atom inversion in this particular complex (Table 3).

In the complexes [ReBr(CO)$_3$(Me$_2$Se)$_2$] and [ReI(CO)$_3$(Me$_2$Se)$_2$], the chemical shift differences in the protons of the two anisochronous methyl groups were sufficiently large to permit full DNMR studies which produced reliable values for the selenium inversion energies (Table 3). An extra single peak in [ReI(CO)$_3$(Me$_2$Se)$_2$] was temperature invariant, and was presumed due to the *mer*-1 isomer. (The *mer*-2 isomer would have produced two peaks of equal intensity, which would also have been non-temperature variable). This *mer*-1
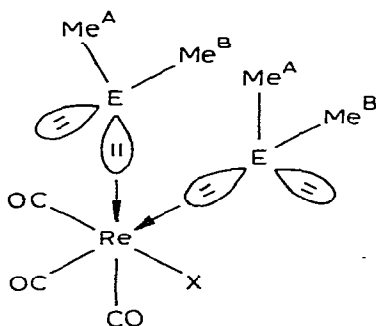

Fig. 2. Configuration of ligand metal bonding with inversion arrested.

TABLE 2

NMR STATIC PARAMETERS OF THE COMPLEXES fac-[ReX(CO)$_3$(Me$_2$E)$_2$]

Complex	Solvent	Temp. (°C)	ν_A [a] (Hz)	p_A	ν_B [a] (Hz)	p_B	T_2^*	Notes
[ReCl(CO)$_3$(Me$_2$S)$_2$] [b]	CD$_2$Cl$_2$	−71	268.7	0.5	263.5	0.5	0.183	^{1}H peak at 251.7 Hz at 25°C
[ReCl(CO)$_3$(Me$_2$Se)$_2$] [c]	CD$_2$Cl$_2$	−13	374.5	0.5	334.4	0.5	0.212	$^2J(^{77}$Se—H) = 8.6 Hz
[ReBr(CO)$_3$(Me$_2$Se)$_2$] [b]	CD$_2$Cl$_2$	−20	255.1	0.5	250.7	0.5	0.424	$^2J(^{77}$Se—H) = 8.7 Hz
[ReI(CO)$_3$(Me$_2$Se)$_2$] [b]	CDCl$_3$	−20	268.1	0.5	255.7	0.5	0.354	^{1}H peak at 250.5 Hz due to *mer* isomer

[a] Shifts relative to Me$_4$Si. [b] ^{1}H data. [c] ^{13}C data.

TABLE 3

ARRHENIUS AND ACTIVATION PARAMETERS FOR SULPHUR AND SELENIUM INVERSIONS FROM COMPUTER-SIMULATED LINE SHAPE FITTINGS

Complex	E_a (kJ mol^{-1})	log$_{10}$ A	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
[ReCl(CO)$_3$(Me$_2$S)$_2$]			48.0		
[ReCl(CO)$_3$(Me$_2$Se)$_2$] [d]	61.8 ± 2.5	12.2 ± 0.4	65.1 ± 4.9 [b]	59.2 ± 2.5	—19.5 ± 8.1
[ReBr(CO)$_3$(Me$_2$Se)$_2$]	72.2 ± 1.3	13.9 ± 0.2	65.5 ± 2.7 [c]	69.8 ± 1.3	14.3 ± 4.6
[ReI(CO)$_3$(Me$_2$Se)$_2$]	68.8 ± 1.6	13.4 ± 0.2	65.1 ± 3.2	66.3 ± 1.6	4.0 ± 5.3

[a] Obtained from coalescence temperature only (212.5 K). [b] 65.7 kJ mol^{-1} obtained from coalescence temperature (315.6 K) of ^{13}C signals. [c] 65.6 kJ mol^{-1} obtained from coalescence temperature. [d] Data obtained from ^{13}C spectra.

isomer has been included in the computer simulation of complete line shape changes. This enabled complete fitting despite slight overlap between the *fac* and *mer* isomers.

The activation parameters for the rhenium(I) complexes studied re-emphasise two important points noted for other metals.

Changes of halogen *cis* to the chalcogen inverting centre have no significant effect on the free energy of activation ($\Delta G^{\ddagger}$) (See Table 3). There is, however, a notable difference in the sulphur and selenium inversion energies of ~17 kJ mol^{-1}, when coordinated to the same metal centre, in this case Re^I.

Two further comparisons concern firstly the isoelectronic and isostructural species [PtMe$_3$X(EMe$_2$)$_2$], which have been studied in an exactly analogous manner [13,14]. In these Pt^{IV} complexes the values of $\Delta G^{\ddagger}$ are ~8 kJ mol^{-1} lower than the corresponding Re^I complexes. As the latter complexes may be considered less sterically crowded than the platinum complexes, then the higher inversion energies on rhenium must be regarded as of electronic origin and associated with the different natures of the Re^I ← S(Se) and Pt^{IV} ← S(Se) bonds.

Secondly, in the closely related cyclic complexes [Re(CO)$_3$X(CH$_3$ECH$_2$-CH$_2$ECH$_3$)] (X = Cl, Br, E = S and Se), the activation energies ($\Delta G^{\ddagger}$) rise [15] by as much as 18—20 kJ compared to the non-cyclic [Re(CO)$_3$X(Me$_2$E)$_2$] complexes. Such a significant increase would appear to be due to the restraint that the five-membered ring imposes upon the access of the chalcogen atoms to the transition state structures (which ideally involve C—E—C angles of 120°) in the chelate complexes, as opposed to the open chain methyl compounds.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer. NMR spectra were obtained on either a Jeol MH100 or a Jeol PS/PFT-100. A JES-VT-3 variable temperature unit controlled the probe temperature, which was measured by a thermocouple inserted directly into the probe. Measurements of temperature were made immediately before and after recording the spectra and were reliable to ca. ±1°C over the ranges covered. Reactions were performed routinely under an atmosphere of dry nitrogen, and melting points

(uncorrected) were determined using an Electrothermal melting point apparatus.

Dimethylsulphide and dimethylselenide were used as supplied and [{ReX(CO)$_4$}$_2$] (X = Cl and Br) were prepared by reported methods [16].

Preparation of ReI(CO)$_5$

A mixture of Re$_2$(CO)$_{10}$ (3.00 g, 4.60 mmol) and I$_2$ (1.28 g, 5.06 mmol) were heated in an evacuated sealed tube at 130°C for 3 h. The product was sublimed (55°C, 0.01 mmHg/1 day) to condense pure Re(CO)$_5$I (1.3 g, 31%) as colourless crystals. The residue was recrystallized from chloroform to yield pure [{ReI(CO)$_4$}$_2$] (1.6 g, 41%).

Preparation of [ReBr(CO)$_3$(Me$_2$Se)$_2$]

To a suspension of [{ReBr(CO)$_4$}$_2$] (0.300 g, 0.396 mmol) in CHCl$_3$ (10 cm^3) was added Me$_2$Se (0.194 g, 1.782 mmol), and the mixture was stirred under reflux (48 h). The volume of the resulting solution was reduced to 2 cm^3. After filtration this solution was added to petroleum spirit (40—60°C) (2 cm^3) and the mixture slowly cooled to —20°C. White crystals of [ReBr(CO)$_3$-(Me$_2$Se)$_2$] were deposited (0.320 g, 71%) (Table 1).

The analogous chloro and iodo complexes were obtained in an analogous manner; in the case of the iodo complex, however, seven days heating were required to remove the last traces of [{Re(CO)$_4$I}$_2$], as shown from infrared spectra of the reacting mixture.

Preparation of [ReCl(CO)$_3$(Me$_2$S)$_2$]

Re(CO)$_5$Cl (2.00 g, 5.3 mmol) and Me$_2$S (4 g, excess) were heated in an evacuated sealed tube (100°C/72 h). Excess ligand was removed (20°C/0.01 mmHg), and the residue recrystallized from chloroform/petroleum spirit (40—60°C) to yield pure product (1.75 g, 74%) (Table 1).

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