A Nuclear Magnetic Resonance Study of Pyramidal Atomic Inversion in Complexes of Tricarbonylrhenium(I) Halides with Saturated and Unsaturated Thio- and Seleno-ethers: An *X*-Ray Crystal Structure of [ReI(CO)$_3${MeSe(CH$_2$)$_2$SeMe}] *

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Complexes of the type [ReX(CO)$_3$L] [X = Cl, Br, or I; L = MeE(CH$_2$)$_n$EMe (n = 2 or 3, E = S or Se) or MeECH=CHEMe (E = S or Se)] have been prepared and the energy barriers associated with the pyramidal inversions at individual chalcogen atoms calculated using total bandshape dynamic n.m.r. methods. The effects of ring size, conjugation, and the nature of the halogen on barrier energies are discussed.

This paper presents part of our studies on the factors governing the energy barriers to inversion of sulphur and selenium atoms.[1-9] Previous work has shown that dithio- and diselenoethers MeE(CH$_2$)$_n$EMe react with trimethylplatinum(IV) halides to form dinuclear complexes when n = 0 or 1 [4,6] and mononuclear complexes when n = 2 or 3.[4,5] The fluxional properties of analogous complexes containing the mixed chalcogen ligands MeSRSeMe [R = CH$_2$, (CH$_2$)$_2$, or *o*-C$_6$H$_4$] have recently been discussed.[8,9]

We report here the results of a dynamic n.m.r. (d.n.m.r.) study on the isoelectronic and isostructural mononuclear rhenium(I) complexes [ReX(CO)$_3${MeE(CH$_2$)$_n$EMe}] (E = S or Se, n = 2 or 3) and [ReX(CO)$_3$(MeECH=CHEMe)] (E = S or Se). The corresponding complexes with mixed chalcogen ligands will be published elsewhere.[10]

The dynamic behaviour of these rhenium(I) complexes resembles that of the trimethylplatinum(IV) halide analogues. The chalcogen atoms are shown to be inverting essentially independently and, in most cases, all possible invertomer species are detected at low temperatures. In addition, the crystal structure and packing arrangement of the complex [ReI(CO)$_3${MeSe(CH$_2$)$_2$SeMe}] is reported.

Experimental

Materials.—The ligands were prepared according to the literature methods: 1,2-bis(methylthio)ethane, b.p. 178 °C (lit.,[11] 181—183 °C); 1,3-bis(methylthio)propane, b.p. 88 °C (12 mmHg) [lit.,[12] 86.5 °C (12 mmHg)]; dimethyl diselenide, b.p. 45 °C (15 mmHg) (lit.,[13] 153 °C); 1,2-bis(methylseleno)ethane, b.p. 88 °C (8 mmHg) (lit.,[14] not reported); 1,3-bis(methylseleno)propane, b.p. 102 °C (8 mmHg) (lit.,[14] not reported); *cis*-1,2-bis(methylthio)ethene, b.p. 80 °C (8—10 mmHg) (lit.,[15] not reported). *cis*-1,2-Bis(methylseleno)ethene was prepared by a method analogous to that reported for 1,2-bis(methylseleno)ethane by using *cis*-1,2-dichloroethene, b.p. 93 °C (10 mmHg) [lit.,[16] 68—69 °C (5 mmHg)]. 100-MHz ^{1}H n.m.r. data: δ 2.20 (Se–Me), $^2J(^{77}$Se–H$)$ = 10.9 Hz; δ 6.79 (–CH=CH–), $^2J(^{77}$Se–H$)$ = 9.5 ,$^3J(^{77}$Se–H$)$ = 12.94 Hz.

Pentacarbonylhalogenorhenium(I),[17] octacarbonyldi-μ-halogeno-dirhenium(I),[18] and hexacarbonyldihalogenobis(tetrahydrofuran)dirhenium(I) [19] were prepared by previously reported methods.

Since the preparations of the complexes were very similar, one representative method for each of the chloride complexes is given below. The bromo- and iodo-derivatives were prepared in an analogous manner, the only exception being that a longer reaction period (*ca.* 72 h) was required for the iodo-complexes.

[1,2-*Bis*(*methylthio*)*ethane*]*tricarbonylchlororhenium*(I). To a solution of pentacarbonylchlororhenium(I) (0.300 g, 0.83 mmol) in chloroform (10 cm^3) was added an excess of 1,2-bis-(methylthio)ethane (0.226 g, 1.66 mmol). After heating the reaction mixture under reflux for *ca.* 24 h, its i.r. spectrum exhibited three new bands in the carbonyl-stretching region, and peaks for the starting material were no longer observed. The solution volume was reduced to *ca.* 2 cm^3 under vacuum and light petroleum (b.p. 40—60 °C) (2 cm^3) added. Cooling this solution to −20 °C overnight gave the product as white crystals. These were washed with light petroleum and dried under vacuum (0.300 g, 82%).

The above complex could also be prepared in good yield by using octacarbonyldi-μ-chloro-dirhenium(I) or hexacarbonyldichlorobis(tetrahydrofuran)dirhenium(I). In these cases the reaction period was reduced to 18 h and 1 h respectively.

Analytical data for the complexes are given in Table 1.

Spectra.—Deuteriochloroform or CD$_2$Cl$_2$ was the solvent in the temperature range −60 to 60 °C. For higher-temperature studies C$_6$D$_5$NO$_2$ was used. N.m.r. spectra were obtained on a JEOL PS/PFT-100 spectrometer operating at 100 MHz. Computations of n.m.r. band shapes were carried out as previously described.[8] Infrared spectra in the metal carbonyl region were recorded in CHCl$_3$ solution on either Perkin-Elmer 299B or 357 spectrometers.

Crystal Data.—C$_7$H$_{10}$IO$_3$ReSe$_2$, M = 613.18, Monoclinic, a = 14.222(4), b = 11.737(3), c = 7.839(6) Å, β = 91.29(4)°, U = 1 326.6 Å^3, space group $P2_1/n$ (no. 14), Z = 4, D_c = 3.07 g cm^{-3}, $F(000)$ = 1 064, μ(Mo-K_α) = 169.9 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å.

The crystal used for *X*-ray work had dimensions 0.600 × 0.162 × 0.075 mm, and was bounded by the six intersecting

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* *fac*-[1,2-Bis(methylseleno)ethane-*SeSe′*]tricarbonyliodorhenium-(I).

Supplementary data available (No. SUP 23378, 12 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: mmHg ≈ 133 Pa.

Table 1. Characterisation of the complexes

Complex	Colour	M.p./°C	Analysis [a]/% C	Analysis [a]/% H	ν(CO) [b]/cm^{-1}
$[ReCl(CO)_3\{MeS(CH_2)_2SMe\}]$	White	132—133	19.45 (19.65)	2.20 (2.35)	2 038, 1 950, 1 902
$[ReBr(CO)_3\{MeS(CH_2)_2SMe\}]$	White	126—128	17.85 (17.8)	2.05 (2.15)	2 038, 1 946, 1 906
$[ReI(CO)_3\{MeS(CH_2)_2SMe\}]$	Pale yellow	138—140	15.9 (16.2)	1.80 (1.95)	2 034, 1 946, 1 906
$[ReCl(CO)_3\{MeS(CH)_2SMe\}]$	White	142—143	19.6 (19.75)	1.90 (1.90)	2 037, 1 957, 1 914
$[ReBr(CO)_3\{MeS(CH)_2SMe\}]$	White	143	17.8 (17.85)	1.65 (1.70)	2 037, 1 957, 1 917
$[ReI(CO)_3\{MeS(CH)_2SMe\}]$	White	143	16.0 (16.25)	1.45 (1.55)	2 035, 1 957, 1 914
$[ReCl(CO)_3\{MeSe(CH_2)_2SeMe\}]$	White	175—177	16.05 (16.1)	1.90 (1.95)	2 042, 1 954, 1 910
$[ReBr(CO)_3\{MeSe(CH_2)_2SeMe\}]$	Pale yellow	135—137	14.85 (14.85)	1.75 (1.80)	2 042, 1 954, 1 910
$[ReI(CO)_3\{MeSe(CH_2)_2SeMe\}]$	Pale yellow	149—151	13.5 (13.7)	1.50 (1.65)	2 034, 1 950, 1 908
$[ReCl(CO)_3\{MeSe(CH)_2SeMe\}]$	White	130	16.15 (16.1)	1.35 (1.55)	2 047, 1 957, 1 912
$[ReBr(CO)_3\{MeSe(CH)_2SeMe\}]$	White	162—163	14.6 (14.9)	1.30 (1.40)	2 047, 1 957, 1 917
$[ReI(CO)_3\{MeSe(CH)_2SeMe\}]$	Light green	162	13.65 (13.75)	1.30 (1.30)	2 040, 1 957, 1 912
$[ReCl(CO)_3\{MeS(CH_2)_3SMe\}]$	White	118—120	21.6 (21.75)	2.65 (2.75)	2 037, 1 945, 1 912
$[ReBr(CO)_3\{MeS(CH_2)_3SMe\}]$	White	133—135	19.6 (19.75)	2.35 (2.50)	2 042, 1 950, 1 914
$[ReI(CO)_3\{MeS(CH_2)_3SMe\}]$	Pale yellow	124—125	17.85 (18.0)	2.10 (2.25)	2 038, 1 948, 1 912
$[ReCl(CO)_3\{MeSe(CH_2)_3SeMe\}]$	White	140—142	17.9 (17.95)	2.35 (2.25)	2 034, 1 938, 1 906
$[ReBr(CO)_3\{MeSe(CH_2)_3SeMe\}]$	Pale yellow	135—137	16.6 (16.55)	2.00 (2.10)	2 038, 1 942, 1 906
$[ReI(CO)_3\{MeSe(CH_2)_3SeMe\}]$	Pale yellow	129—131	15.2 (15.3)	1.75 (1.90)	2 036, 1 944, 1 906

[a] Calculated values are given in parentheses. [b] Infrared spectra were recorded in $CHCl_3$ solution; all carbonyl stretching frequencies were very strong.

faces (001), (00$\bar{1}$), ($\bar{2}$10), (2$\bar{1}$0), (210), and ($\bar{2}\bar{1}$0). The unit-cell parameters were initially determined from oscillation and Weissenberg photographs, and later refined on a Nonius CAD4 diffractometer using the setting angles for 25 reflections [$16 \leqslant \theta(\text{Mo-}K_\alpha) \leqslant 18°$]. The intensities of 3 308 reflections ($\pm h$, k, l; $1.5 \leqslant \theta \leqslant 27°$) were measured on the same diffractometer using Mo-K_α radiation and an ω—2θ scan mode, in a manner described elsewhere.[20] Two standard reflections monitored every hour showed that the crystal and instrument remained quite stable during data collection. The data were corrected for Lorentz polarisation and absorption effects, and merged to obtain 2 856 unique reflections. Of these, 2 288 were considered observed [$F_o > 4\sigma(F_o)$] and were used in the structure analysis.

The structure was solved by Patterson and successive electron-density syntheses, and refined by full-matrix least squares. Having assigned all non-hydrogen atoms with anisotropic temperature factors, the structure was finally refined to $R(=\Sigma\Delta F/\Sigma F_o) = 0.037$ with $R'[=(\Sigma w\Delta F^2/\Sigma wF^2)^{\frac{1}{2}}] = 0.048$. The hydrogen atoms were very poorly defined in difference maps, and these were ignored. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.000\,45|F_o|^2]$ was applied and this gave virtually flat analyses of variance with sinθ and $(F_o/F_{\text{max.}})^{\frac{1}{2}}$. A final difference electron-density map was essentially featureless. Neutral atom scattering factors for Re, I, and Se were taken from tables,[21] and corrected for anomalous dispersion using published [22] values of $\Delta f'$ and $\Delta f''$; values for O and C were also taken from the literature.[23] The final atomic positional parameters are given in Table 5. The computers and programs used were those described previously.[24]

Results

The inverting systems reported here are analogous to those for the trimethylplatinum(IV) complexes [4,5] and hence only a brief description of the spectra is given.

The five-membered ring complexes $[ReX(CO)_3\{MeE(CH_2)_2EMe\}]$ will be discussed first. The two sulphur or selenium atoms are centres of chirality and thus, in the absence of any internal rate process, four diasteroisomers of the complexes may exist, namely two distinct *meso* forms and a degenerate pair of DL forms (Figure 1). Evidence for these invertomers comes from the low-temperature spectra of the complexes, and the spectra of $[ReBr(CO)_3\{MeS(CH_2)_2SMe\}]$ illustrated in Figure 2 may be taken as typical. At *ca.* −30 °C the S-Me region consisted of four lines which are attributed to the three distinct invertomers shown in Figure 1. On warming the sample, coalescence of these signals occurred until at *ca.* 25 °C a single averaged line was observed. These changes were without doubt due to the varying rate of pyramidal inversion at the sulphur atoms.

The assignments of the lines as shown in Table 2 and Figure

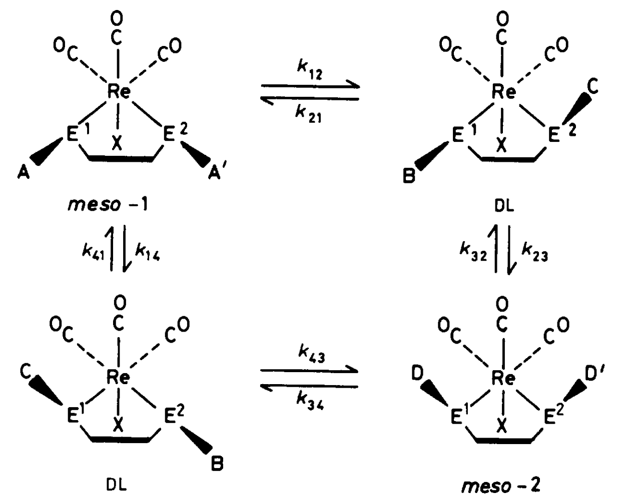


Figure 1. Interconversion of [ReX(CO)$_3$L] isomers by independent inversion of E atoms

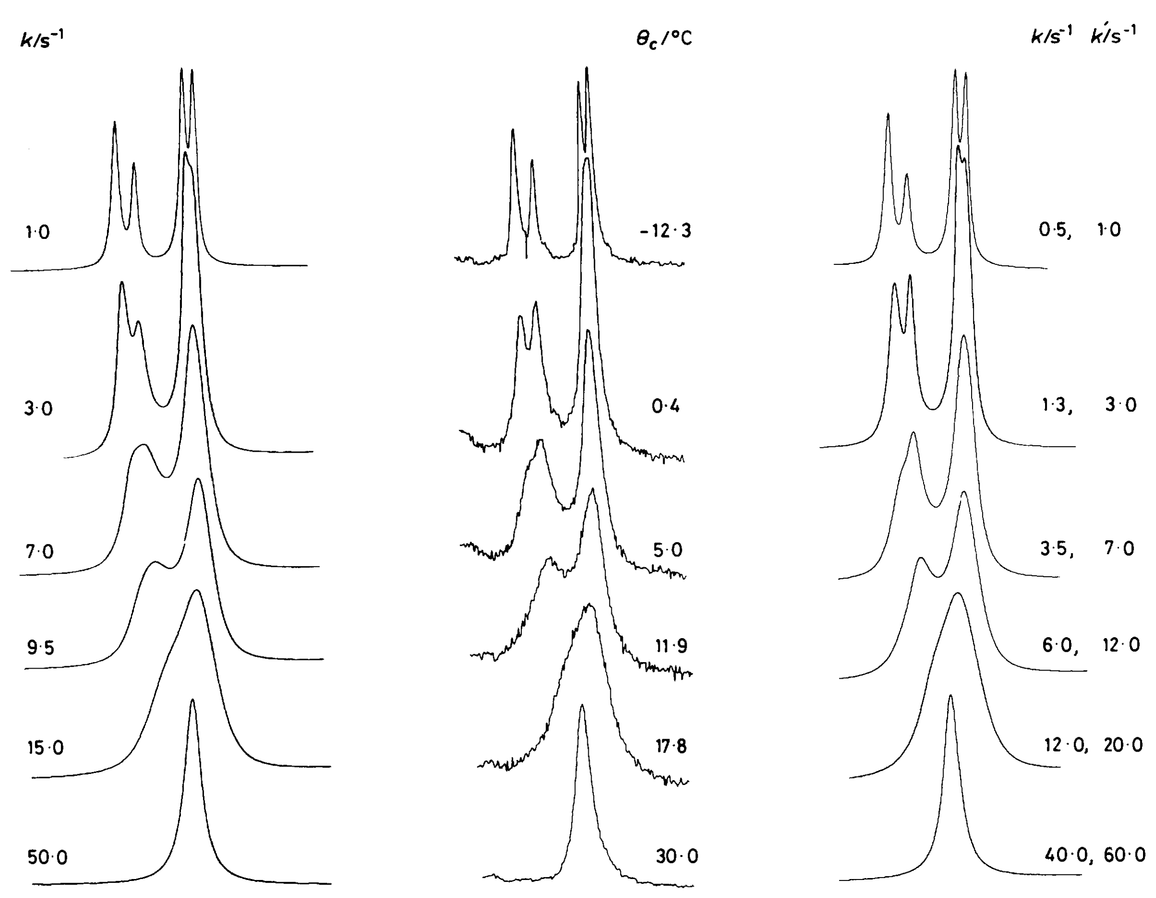


Figure 2. Experimental and theoretical spectra of [ReBr(CO)$_3${MeS(CH$_2$)$_2$SMe}] showing the effect of using one or two rate constants to simulate sulphur inversion

3 were made on the basis of the observed trends in the chemical shifts and invertomer populations. It was found that the E–Me protons situated below the averaged E–Re–E plane were very sensitive to the nature of the halogen atom. For example, in the series [ReX(CO)$_3${MeSe(CH$_2$)$_2$SeMe}], when X varied from Cl to I, the chemical shift ν_A increased by 20.0 Hz whereas ν_C increased by only 2.6 Hz. Moreover, increasing the size of the halogen atom appeared to favour the less sterically restricted *meso*-2 isomer at the expense of the *meso*-1 and DL isomers (Figure 3). The methylene regions of the spectra of all the complexes exhibited predictably complex absorptions at most temperatures, and were not analysed in any detail, as no additional information would have been obtained.

These dramatic changes in invertomer populations prompted us to examine the *X*-ray crystal structure of the complex [ReI(CO)$_3${MeSe(CH$_2$)$_2$SeMe}]. The molecular structure shown in Figure 4 indicates the atom-numbering system used. Important bond lengths and angles are presented in Table 3 with the results of selected least-squares plane and dihedral-angle calculations in Table 4.

The co-ordination about the rhenium atom is distorted octahedral, with the iodide group *cis* to both selenium atoms of the chelate ring. The two methyl groups on the selenium atoms are positioned away from the bulky iodine atom. This structure represents the *meso*-2-isomer which predominates in solution. The structure is very similar to the related compound [ReBr(CO)$_3${Me(H)N(CH$_2$)$_2$N(H)Me}], whose structure we have reported recently.[24] In both compounds the chelate ring adopts only one conformer (λ-*gauche*), and the torsional angles across the ligand C–C bond, *i.e.* Se–CH$_2$–CH$_2$–Se (59.1°) and N–CH$_2$–CH$_2$–N (57.3°), are nearly equal. This contrasts with the structure of [ReBr(CO)$_3$-{Me$_2$N(CH$_2$)$_2$NMe$_2$}] [25] where two conformers are present in the crystal.

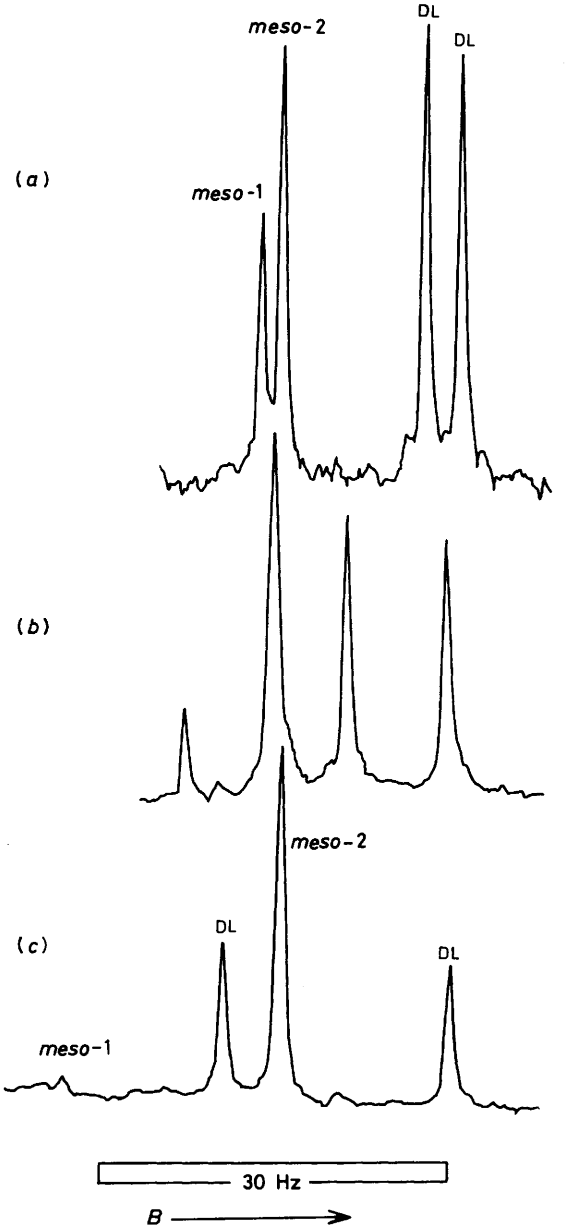


Figure 3. Low-temperature ^1H n.m.r. spectra of [ReX(CO)$_3${MeSe(CH$_2$)$_2$SeMe}] showing the halogen dependence of invertomer populations on the ligand methyl region. Lines are labelled according to Figure 1. X = Cl (*a*), Br (*b*), and I (*c*)

The Re–I bond length [2.812(1) Å] agrees very well with the value (2.81 Å) predicted on the basis of the covalent radii of I (1.33 Å)[26] and Re (1.48 Å), the latter obtained by subtracting the covalent radius of Br (1.14 Å)[26] from the mean Re–Br distance found in the two bromo-compounds mentioned above. However, the mean Re–Se bond length (2.595 Å) is *ca.* 0.05 Å shorter than the predicted value (2.65 Å) taking a covalent radius of (1.17 Å)[26] for Se. Other bond lengths and angles are normal. The shortest intermolecular contact is 3.078 Å between O(1) and O(3) ($1 - x, -y, -z$), which indicates fairly tight packing of the molecules in the unit cell. A packing diagram is presented in Figure 5.

Observation of the experimental ^1H n.m.r. spectra (Figure 2) reveals that, as pyramidal inversion becomes rapid, the different environments of the E–Me groups average out. This can readily be seen by considering the cyclic scheme shown in Figure 1, in which inversion is considered to occur at each E atom independently in an uncorrelated manner. Due to the likely low probability of synchronous inversion at both E atoms, direct interconversion between the *meso*-1 and *meso*-2 invertomers and between the DL pair was excluded, *i.e.* $k_{13} = k_{24} = 0$.

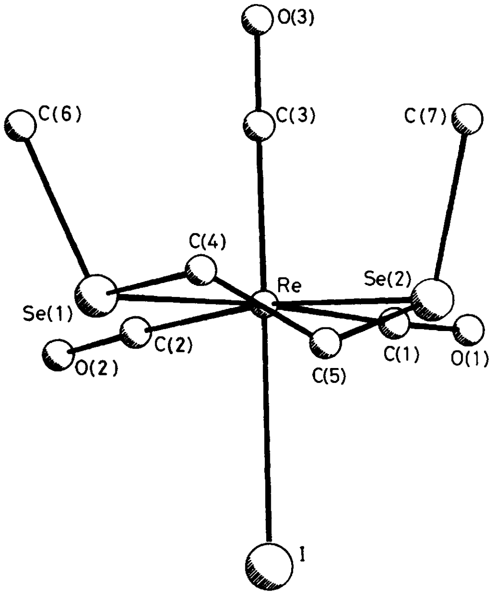
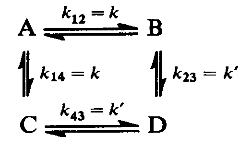


Figure 4. Molecular structure of *fac*-[ReI(CO)$_3${MeSe(CH$_2$)$_2$SeMe}] showing the atom numbering and puckering of the chelate ring

Thus, the dynamic process under investigation involves interconversion between four chemical configurations each consisting of two spins. However, since no spin couplings were observed between the E methyls in the same isomer the spin problem could be simplified as depicted in Scheme 1.



Scheme 1.

Before computing the E–Me band shapes, the static parameters, namely chemical shifts, invertomer populations, and effective transverse relaxation times, T_2*, were measured as accurately as possible over a wide temperature range where the inversion process was slow. With the exception of the complex [ReBr(CO)$_3${MeSe(CH$_2$)$_2$SeMe}] in which the isomer populations varied with temperature, these parameters were essentially temperature invariant.

The experimental and computer-synthesised spectra shown in Figure 2 demonstrate the effects of using either a single magnitude of rate constant[5] (*i.e.* making the assumption $k = k'$) or two independent values.[9] It can be clearly seen that the spectra can distinguish *two* rate constants only at certain low temperatures, notably 0.4 and 5 °C. As the temperature is raised the spectra can be fitted equally well by using one or two rate constants.

In the five-membered ring complexes with the unsaturated

Table 2. Low-temperature ^{1}H n.m.r. data for the E–Me region of complexes $[ReX(CO)_3L]$

Complex			*meso*-1		DL			*meso*-2		
X	L	θ_c/°C	ν_A [a]	p_A [b]	ν_B	ν_C	$p_B + p_C$	ν_D	p_D	T_2 *
Cl	$MeS(CH_2)_2SMe$	−43.0	268.8	26.1	255.8	265.6	57.6	280.6	16.3	0.367
Br		−43.7	276.0	12.9	263.5	267.1	57.8	281.6	29.3	0.275
I		−58.1	288.6	5.8	276.1	268.2	52.8	282.7	41.4	0.245
Cl	MeSCH=CHSMe	−78.8	287.8 †	45.5	283.6	281.1	19.2	294.9	35.3	0.215
		−71.4 [c]	694.6	46.0	687.5	693.3	20.0	704.3	34.0	0.250
Br		−72.4	295.4 †	35.8	289.3	283.4	15.2	294.2	49.0	0.220
		−82.5 [c]	693.7	35.8	688.1	692.8	15.2	704.9	49.0	0.286
I		−78.2	307.6 †	11.6	301.3	284.1	16.4	293.6	72.0	0.188
Cl	$MeSe(CH_2)_2SeMe$	12.8	254.0	16.9	239.7	236.6	54.6	252.2	28.5	*c*
Br		8.3	261.5	8.8	247.1	238.4	54.6	253.6	36.6	0.318
I		8.0	274.0	3.6	260.0	239.2	42.6	253.9	53.8	0.458
Cl	MeSeCH=CHSeMe	26.0	270.9	31.1	262.3	256.1	27.5	267.7	41.4	0.327
		26.0 [c]	756.4	31.1	746.3	758.7	27.5	762.6	41.4	0.330
Br		28.9	279.1	18.8	270.5	255.6	24.2	266.1	57.0	0.318
		5.6 [c]	755.4	14.6	747.0	760.0	25.4	765.9	60.0	0.286
I		26.0	292.2	7.2	283.8	255.1	19.2	264.6	73.6	0.240
		−11.5	751.1	7.2	744.8	758.2	19.2	764.0	73.6	0.573
Cl	$MeS(CH_2)_3SMe$	−50.0		*ca.* 0	276.0	264.0	*d*	270.0	*d*	*d*
Br		−50.0		*ca.* 0	278.0	266.0	*d*	270.0	*d*	*d*
I		−50.0		*ca.* 0	280.0	266.0	*d*	268.0	*d*	*d*
Cl	$MeSe(CH_2)_3SeMe$	−60.0	265.3	*d*	257.8	250.2	*d*	254.0	*d*	*d*
Br		−60.0	264.4	*d*	258.6	253.2	*d*	255.7	*d*	*d*
I		−60.0	263.3	*d*	260.1	257.5	*d*	258.7	*d*	*d*

[a] Chemical shifts ν_i/Hz measured relative to $SiMe_4$; solvent was $CDCl_3$ except where indicated (†) when CD_2Cl_2 was used. [b] Isomer populations (%) were slightly temperature dependent. [c] Data refer to the olefinic protons ($^2J_{BC}$ = 6.0—6.2 Hz). [d] Not measured.

Table 3. Intramolecular interatomic distances (Å) and interbond angles (°) with estimated standard deviations in parentheses

Re–I	2.812(1)	Re–C(1)	1.954(10)
Re–Se(1)	2.593(1)	Re–C(2)	1.921(10)
Re–Se(2)	2.597(1)	Re–C(3)	1.900(9)
C(1)–O(1)	1.115(11)	Se(1)–C(4)	1.970(9)
C(2)–O(2)	1.137(11)	Se(1)–C(6)	1.946(11)
C(3)–O(3)	1.149(11)	Se(2)–C(5)	1.989(9)
		Se(2)–C(7)	1.991(11)
		C(4)–C(5)	1.469(14)
I–Re–Se(1)	84.1(1)	Se(1)–Re–Se(2)	85.2(1)
I–Re–Se(2)	81.8(1)	Se(1)–Re–C(1)	175.4(3)
I–Re–C(1)	91.6(3)	Se(1)–Re–C(2)	91.8(3)
I–Re–C(2)	90.2(3)	Se(1)–Re–C(3)	93.0(3)
I–Re–C(3)	176.4(3)	Se(2)–Re–C(1)	92.6(3)
C(1)–Re–C(2)	89.8(4)	Se(2)–Re–C(2)	171.7(3)
C(1)–Re–C(3)	91.3(4)	Se(2)–Re–C(3)	96.0(3)
C(2)–Re–C(3)	91.9(4)		
Re–Se(1)–C(4)	102.3(3)	Re–Se(2)–C(5)	100.9(3)
Re–Se(1)–C(6)	107.7(4)	Re–Se(2)–C(7)	108.9(4)
C(4)–Se(1)–C(6)	96.8(5)	C(5)–Se(2)–C(7)	97.5(5)
Re–C(1)–O(1)	176.1(8)	Se(1)–C(4)–C(5)	113.8(7)
Re–C(2)–O(2)	177.7(10)	Se(2)–C(5)–C(4)	112.3(6)
Re–C(3)–O(3)	177.8(9)		

Table 4. Least-squares planes in the form $Ax + By + Cz = D$, where x, y, z are fractional co-ordinates. Deviations (Å) of relevant atoms are given in square brackets

Plane (1) through Re, Se(1), and Se(2)

$$0.8451x + 9.1015y + 4.9167z = 2.8938$$

[C(4) −0.220, C(5) 0.529, C(6) −1.764, C(7) −1.879]

Plane (2) through Re, C(4), and C(5)

$$-6.5126x + 7.3561y + 5.0565z = -0.2299$$

Angle between plane (1) and (2) = 30.8°, torsion angle between the Se atoms across the C(4)–C(5) bond = 59.1°.

Table 5. Fractional co-ordinates (Re, I, Se × 10^5; O, C × 10^4) of the non-hydrogen atoms with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Re	38 418(2)	18 464(3)	18 073(4)
I	39 942(5)	39 322(5)	35 555(8)
Se(1)	24 591(7)	28 274(8)	2 290(12)
Se(2)	48 671(7)	29 174(8)	−3 515(12)
O(1)	5 509(5)	819(7)	3 759(10)
O(2)	2 603(6)	932(7)	4 610(10)
O(3)	3 657(6)	−350(7)	−248(10)
C(1)	4 920(7)	1 229(8)	3 046(11)
C(2)	3 049(8)	1 268(8)	3 543(13)
C(3)	3 715(7)	489(8)	502(12)
C(4)	3 066(7)	3 572(9)	−1 702(13)
C(5)	3 975(7)	4 071(7)	−1 258(13)
C(6)	1 803(8)	1 667(10)	−1 099(18)
C(7)	4 956(10)	1 986(11)	−2 463(16)

ligands MeECH=CHEMe analogous spectral changes were observed in the E–Me region. In addition, these complexes possess an advantage in that the effects of chalcogen inversion are also observable in the vinyl region which at low temperatures consists of single lines for the two *meso* isomers and an AB quartet for the degenerate DL pair. Experimental and computer-synthesised spectra of both regions are shown in Figure 6 with the appropriate static parameters given in Table 2.

The low-temperature (*ca.* −50 °C) ^{1}H n.m.r. spectra of the complexes $[ReX(CO)_3\{MeE(CH_2)_3EMe\}]$ revealed the presence of three peaks in the E–Me region when E = S and four when E = Se. The assignments of these peaks are listed in Table 2. As these signals overlapped with the methylene region, no accurate assessment of invertomer populations could be made and hence no complete band-shape fittings were possible.

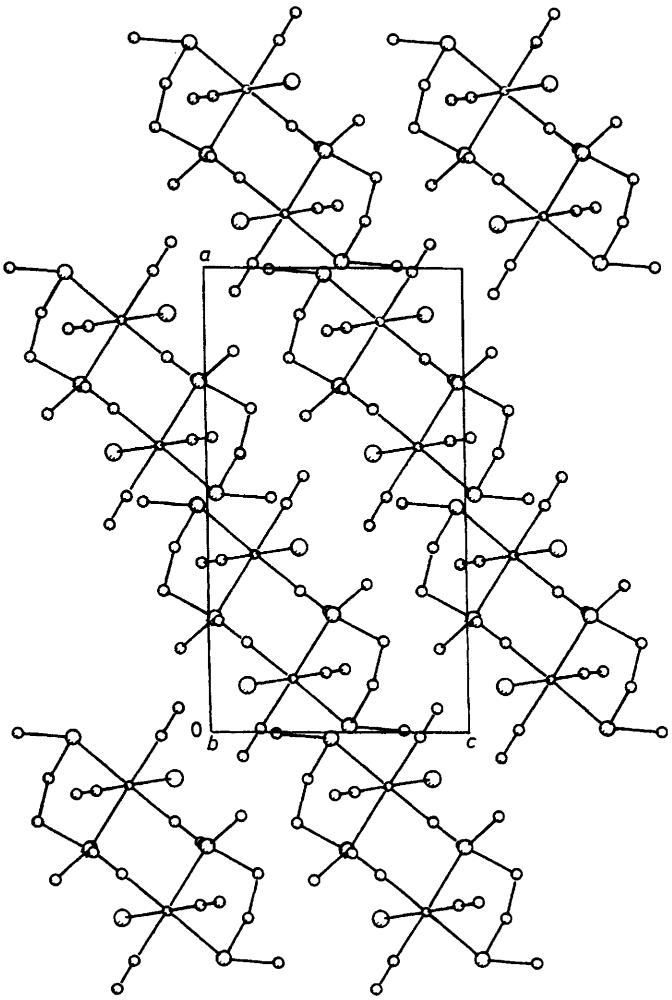


Figure 5. Packing of the molecules in the unit cell looking down *b*

On warming the samples, coalescence of the signals occurred at *ca.* −30 °C for the sulphur complexes and at *ca.* 50 °C for the selenium complexes. This large variation in coalescence temperature suggests that chalcogen inversion and not chair-to-chair ring reversal is the dominant cause of the spectral changes.

The apparent absence of the *meso*-1 invertomer (Figure 1) in the sulphur complexes is thought to be due to the strong interaction of the S–Me groups with the halogen atom. The presence of this invertomer in the selenium complexes can be explained on the basis of the greater Re–Se bond length, which results in decreased steric hindrance between the selenium methyls and the halogen atom. Complementary evidence has been obtained from the low-temperature ^{13}C n.m.r. spectra of the complexes.

Discussion

The energy-barrier data associated with the pyramidal atomic inversion process are collected in Table 6. Comparison of these values (especially $\Delta G^‡$, which is the least prone to systematic error) reveals that these barriers are considerably lower than those for sulphoxides [27] and selenoxides,[28] a factor attributable to appreciable $(p\text{–}d)\pi$ bonding between the ligand and metal in the transition state.[1,2,9]

These data are consistent with earlier results, in that the inversion barriers at selenium are higher than those at sulphur, and that changes of halogen *cis* to the inverting centre have a negligible effect on the overall barrier height.

Comparison of the data for the saturated five-membered ring complexes with those for the isoelectronic and isostructural trimethylplatinum(IV) complexes [5] shows that the inversion barriers at sulphur are 2—3 kJ mol^{-1} higher in the rhenium(I) complexes, while the corresponding barriers at selenium are *ca.* 12 kJ mol^{-1} higher. These greater inversion energies must be associated with the different natures of the $Re^{I}\leftarrow S(Se)$ and $Pt^{IV}\leftarrow S(Se)$ bonds.

Replacement of the saturated aliphatic backbone of the ligand by the unsaturated moiety –CH=CH– lowers the $\Delta G^‡$ values for sulphur and selenium inversion by *ca.* 9—12 and 6—8 kJ mol^{-1} respectively. This is certainly the result of $(p\text{–}p)\pi$ conjugation between the chalcogen lone pair and the ligand backbone, which is more effective in the planar transition state than in the pyramidal ground state. These results suggest that the $(3p\text{–}2p)\pi$ conjugation in the case of sulphur inversion is more effective than the $(4p\text{–}2p)\pi$ conjugation associated with selenium inversion.

Although no accurate data have been obtained for chalcogen inversion in the six-membered ring complexes, we estimate on the basis of coalescence temperature measurements that these barriers will be considerably lower than for the five-membered ring analogues. This trend would parallel that found in the tri-

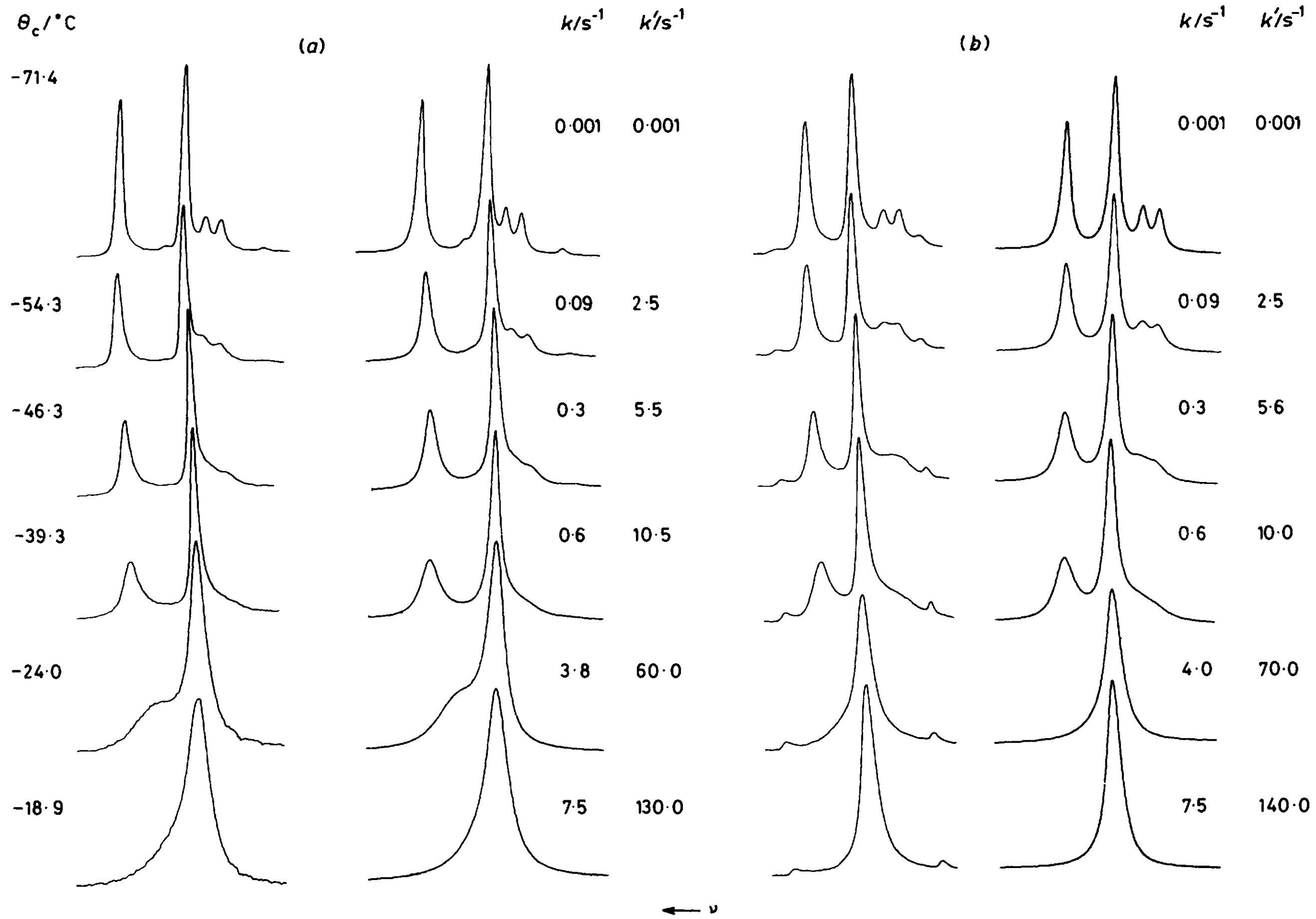


Figure 6. Experimental and computer-synthesised spectra of [ReCl(CO)$_3$(MeSCH=CHSMe)] showing the effects of sulphur inversion on both the vinyl (*a*) and methyl (*b*) regions

Table 6. Arrhenius and thermodynamic activation parameters for sulphur and selenium inversion in complexes of tricarbonylrhenium(I) halides

Complex	Inversion	E_a/kJ mol^{-1}	$\log_{10}A$	$\Delta G^‡$ [a]/kJ mol^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
[ReCl(CO)$_3${MeS(CH$_2$)$_2$SMe}]	S	62.3 ± 2.7	12.3 ± 0.5	65.1 ± 0.1	59.9 ± 2.7	−17.6 ± 9.2
[ReBr(CO)$_3${MeS(CH$_2$)$_2$SMe}]	S^1 [b]	69.4 ± 2.6	13.5 ± 0.5	65.2 ± 0.2	67.0 ± 2.6	6.3 ± 9.3
	S^2 [c]	65.1 ± 2.4	13.0 ± 0.4	63.9 ± 0.2	62.7 ± 2.4	−3.9 ± 8.4
[ReI(CO)$_3${MeS(CH$_2$)$_2$SMe}]	S	66.9 ± 3.5	12.8 ± 0.6	66.7 ± 0.1	64.4 ± 3.5	−7.6 ± 11.8
[ReBr(CO)$_3${MeSe(CH$_2$)$_2$SeMe}]	Se	98.8 ± 5.3	14.9 ± 0.7	86.7 ± 1.0	95.8 ± 5.3	30.4 ± 14.4
[ReI(CO)$_3${MeSe(CH$_2$)$_2$SeMe}]	Se	78.2 ± 3.2	11.6 ± 0.4	84.5 ± 0.6	75.1 ± 3.2	−31.5 ± 8.7
[ReCl(CO)$_3$(MeSCH=CHSMe)]	S^1	57.5 ± 1.0	12.7 ± 0.2	58.1 ± 0.2	55.5 ± 1.0	−9.0 ± 4.1
	S^1 [d]	60.8 ± 1.2	13.4 ± 0.3	57.5 ± 0.3	58.8 ± 1.2	4.3 ± 5.0
	S^2	52.8 ± 1.6	13.0 ± 0.4	51.9 ± 0.4	50.9 ± 1.6	−3.4 ± 6.7
	S^2 [d]	55.1 ± 1.0	13.4 ± 0.2	51.6 ± 0.3	53.0 ± 1.0	4.9 ± 4.1
[ReBr(CO)$_3$(MeSCH=CHSMe)]	S^1 [d]	60.2 ± 1.0	13.2 ± 0.2	57.7 ± 0.3	58.2 ± 1.0	1.8 ± 4.1
	S^2 [d]	54.3 ± 0.8	13.2 ± 0.2	51.8 ± 0.3	52.3 ± 0.8	1.5 ± 3.2
[ReI(CO)$_3$(MeSeCH=CHSeMe)] [e]	Se^1	79.0 ± 0.8	13.2 ± 0.1	76.3 ± 0.1	76.1 ± 0.7	−0.8 ± 2.1
	Se^2	73.9 ± 1.4	12.9 ± 0.2	73.6 ± 0.2	71.2 ± 1.4	−8.1 ± 4.2

[a] Calculated at 298.16 K. [b] *meso*-1 ⟶ DL. [c] DL ⟶ *meso*-2. [d] Computations performed on olefinic region of the spectra.

methylplatinum(IV) complexes,[5] and also in complexes with inverting nitrogen atoms incorporated into a ring.[29] The lowering of inversion energies on increasing ring sizes is attributable to a stabilisation of the transition state relative to the ground state by an amount related to the angle constraint.

A further comparison may be made with the complexes [ReX(CO)$_3$(Me$_2$E)$_2$] (X = Cl, Br, or I; E = S or Se).[30] The pyramidal atomic inversion barriers in these complexes are *ca.* 18—20 mol^{-1} lower than those for the cyclic complexes. This difference in energy is attributable to the constraint that the five-membered ring imposes on the access of the chalcogen atoms to the transition-state structures in the chelate complexes as opposed to the open-chain methyl compounds.

In all complexes the inversion process was shown to be non-dissociative in nature since a separate ^{1}H n.m.r. signal was observed for added free ligand at temperatures well above the coalescence point.

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