Nuclear Magnetic Resonance Studies of Pyramidal Inversion in Complexes of Tricarbonylrhenium(I) Halides with Aliphatic and Aromatic Mixed Thio–Seleno Ethers

Edward W. Abel, Suresh K. Bhargava, Kenneth Kite, Keith G. Orrell,* Vladimir Šik, and Bruce L. Williams
Department of Chemistry, University of Exeter, Exeter EX4 4QD

Mixed-chalcogen ligand complexes of type *fac*-[ReX(CO)$_3$(MeSZSeMe)] (X = Cl, Br, or I; Z = CH$_2$CH$_2$ or *o*-C$_6$H$_4$) have been prepared and their temperature-dependent ^{1}H n.m.r. spectra studied. Pyramidal S and/or Se inversions were observed in all cases and quantitatively assessed for the complex *fac*-[ReBr(CO)$_3${*o*-MeS(C$_6$H$_4$)SeMe}] and the dithio-analogues *fac*-[ReX(CO)$_3${*o*-MeS(C$_6$H$_4$)SMe}] (X = Cl, Br, or I). The effects of π conjugation and halogen type on the barrier energies are discussed.

We have previously [1] reported the energy barriers associated with pyramidal inversions at individual S or Se atoms in complexes of tricarbonylrhenium(I) halides with saturated and unsaturated thio- and seleno-ethers, namely *fac*-[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)]. The dynamic behaviour of these rhenium(I) complexes resembles that of the analogous trimethylplatinum(IV) halide complexes on which we have reported in detail.[2,3] The PtXMe$_3$ moiety was recently [4] shown to form stable complexes with mixed S/Se ligands. In such species it proved possible to study pyramidal inversion of both chalcogens in a single experiment.[4] We have now synthesised complexes of ReX(CO)$_3$ with mixed S/Se co-ordinating ligands and report herein their variable-temperature n.m.r. properties. As an aid to interpreting the complicated spectra of *fac*-[ReX(CO)$_3${*o*-MeS(C$_6$H$_4$)SeMe}] we also carried out full dynamic n.m.r. studies on the dithio-analogues *fac*-[ReX(CO)$_3${*o*-MeS(C$_6$H$_4$)SMe}]. We compare the pyramidal inversion energies with those in the analogous homochalcogen ligand complexes of ReX(CO)$_3$ [1] and PtXMe$_3$.[3] The variation of barrier energies in changing from an aliphatic through an aromatic to an olefinic ligand backbone is also discussed and compared with trends observed in palladium(II) and platinum(II) complexes.[5]

Experimental

Materials.—1-Methylseleno-2-methylthioethane, MeSCH$_2$CH$_2$SeMe, was prepared as previously,[4] by an analogous method to that of methylseleno(methylthio)methane [6] using an excess of β-chloroethyl methyl sulphide. 1,2-Bis(methylthio)benzene, *o*-MeS(C$_6$H$_4$)SMe,[7] was prepared by methylation (Me$_2$SO$_4$–NaOH in methanol) of *o*-methylthiobenzenethiol.[4] *o*-Methylselenothioanisole, *o*-MeSe(C$_6$H$_4$)SMe, was prepared by a literature method.[8]

All the complexes were prepared by treating [{ReX(CO)$_4$}$_2$] or [ReX(CO)$_3$(thf)] (thf = tetrahydrofuran) with an excess of the ligand and refluxing in chloroform until the i.r. spectrum of the reaction mixture showed the reaction to be complete, three new carbonyl-stretching modes being observed while those for the starting material had vanished. The thf complex produced a more rapid reaction (complete in 2 h compared to 12 h). All the complexes were colourless, white, or pale yellow, crystalline solids, which were quite stable in air but slowly decomposed in solution. Analytical and i.r. data are reported in Table 1.

N.M.R. Spectra.—A JEOL PS/PFT-100 spectrometer operating at 100 MHz in the Fourier-transform mode was used for most of the ^{1}H studies. Some ambient-temperature 400-MHz ^{1}H spectra were obtained at the University of Warwick. Deuteriochloroform or CD$_2$Cl$_2$ was used as solvent for all the complexes. The complex [ReBr(CO)$_3${*o*-MeS(C$_6$H$_4$)SeMe}] was also studied in the mixed solvent C$_6$D$_5$NO$_2$–C$_6$D$_6$ at above-ambient temperatures. Computations of total n.m.r. band shapes were carried out as previously described,[6] and matchings of experimental and theoretical spectra were performed visually. Activation parameters were based on standard least-squares fittings of Arrhenius and Eyring plots. Errors quoted are root-mean-square (r.m.s.) errors, those for $\Delta G^‡$ being defined according to Binsch and Kessler.[9]

Results

All the complexes in Table 1 exhibit three strong, similar intensity, carbonyl-stretching frequencies in the near-i.r. region. The complexes may exist as either meridional or facial isomers, but *three* CO bands are expected both for the C_s symmetry of the *mer* isomers ($2A' + A''$) and also for the C_s (homochalcogen) or C_1 (heterochalcogen) symmetries of the *fac* isomers. However, the similar intensities of the three CO bands is firm evidence for the *fac* isomer.[10] Further support for this conclusion can be obtained from the high-temperature n.m.r. spectra of the homochalcogen complexes where a *single* SMe proton signal is observed in the limit of rapid sulphur inversions, indicating a mirror plane bisecting the SReS bond angle. No such argument can be applied to the mixed S/Se ligand complexes, but chemical reasoning points to them also being *fac* isomers.

fac-[ReX(CO)$_3${MeS(CH$_2$)$_2$SeMe}] *Complexes.*—The S and Se atoms in these five-membered ring complexes are chiral centres and therefore, in the absence of any internal rearrangement process, four doubly degenerate DL isomers can exist (Figure 1). The situation is analogous to that discussed for the mononuclear trimethylplatinum(IV) halide complexes.[4] At low temperatures (*ca.* −70 °C) the 100-MHz ^{1}H spectra showed evidence for these four individual invertomers, but the spectra were too complex to be interpreted. The 400-MHz ^{1}H spectra clearly indicated eight chalcogen-methyl signals but these overlapped with the very complex ligand-methylene absorptions and prevented any detailed analysis.

fac-[ReX(CO)$_3${*o*-MeE(C$_6$H$_4$)E′Me}].—The problem of overlapping signals does not arise in the above aromatic ligand complexes when E = S and E′ = Se. However, the assignment of the signals to the eight different E-methyl environments was far from straightforward and recourse was

Table 1. Characterisation data of complexes of tricarbonylrhenium(I) halides

Complex	Colour	M.p./°C	Analysis [a] (%)		$\tilde{\nu}$(CO) [b]/cm^{-1}
			C	H	
$[ReCl(CO)_3\{MeS(CH_2)_2SeMe\}]$	White	194	17.7 (17.45)	2.10 (2.10)	2 042, 1 951, 1 910
$[ReBr(CO)_3\{MeS(CH_2)_2SeMe\}]$	White	166—168	16.05 (16.2)	1.85 (1.95)	2 042, 1 952, 1 912
$[ReI(CO)_3\{MeS(CH_2)_2SeMe\}]$	Yellow	166 [c]	14.55 (14.7)	1.60 (1.70)	2 044, 1 956, 1 912
$[ReCl(CO)_3\{o\text{-}MeS(C_6H_4)SMe\}]$	Colourless	146	27.6 (27.75)	2.25 (2.10)	2 047, 1 957, 1 914
$[ReBr(CO)_3\{o\text{-}MeS(C_6H_4)SMe\}]$	White	158	25.4 (25.4)	2.00 (1.95)	2 048, 1 957, 1 917
$[ReI(CO)_3\{o\text{-}MeS(C_6H_4)SMe\}]$	Yellow	163	23.4 (23.3)	1.85 (1.80)	2 042, 1 957, 1 917
$[ReCl(CO)_3\{o\text{-}MeS(C_6H_4)SeMe\}]$	White	152	25.45 (25.4)	1.90 (1.95)	2 045, 1 957, 1 914
$[ReBr(CO)_3\{o\text{-}MeS(C_6H_4)SeMe\}]$	White	143	23.65 (23.3)	1.80 (1.75)	2 042, 1 957, 1 915
$[ReI(CO)_3\{o\text{-}MeS(C_6H_4)SeMe\}]$	Yellow	195	21.9 (21.5)	1.65 (1.65)	2 042, 1 957, 1 917

[a] Theoretical values in parentheses. [b] I.r. spectra recorded in $CHCl_3$. All bands quoted are very strong. [c] Decomposes.

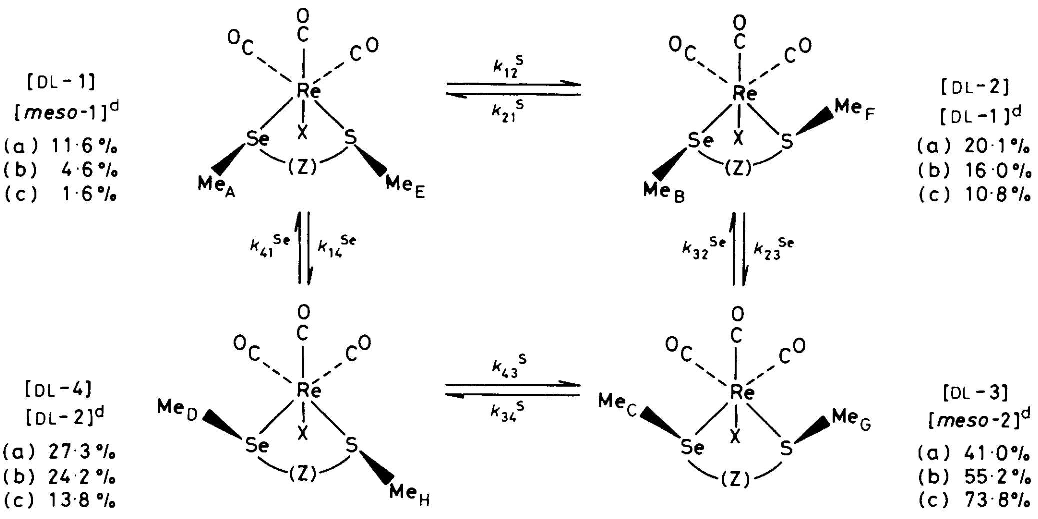


Figure 1. Interconversion of the diastereoisomers of $[ReX(CO)_3(MeSeZSMe)]$ (X = Cl, Br, or I; Z = CH_2CH_2 or $o\text{-}C_6H_4$) as a result of chalcogen inversion. Percentage populations refer to the complex with X = Cl (a), Br (b), and I (c) at *ca.* −70 °C. The isomer labelling for the homochalcogen complexes is also shown (d)

made to the dithioether ligand analogues (E = E′ = S). Chemical shift and invertomer population data for the latter complexes are given in Table 2. From these data it will be seen that the assignments of the mixed-chalcogen complexes can be firmly established. The assignments reported in Table 2 for the mixed S/Se ligand complexes are shown pictorially in Figure 2, where the variations of chemical shifts and invertomer populations with halogen are clearly indicated. The labelling of the signals is in accordance with Figure 1. Changing the halogen from chloro to iodo favours the DL-3 and DL-4 species but the sequence of invertomer populations, *i.e.* DL-3 > DL-4 ⩾ DL-2 > DL-1, is not altered. This demonstrates the strong preference of the SeMe group to occupy the least sterically hindered position, namely *trans* to the halogen. By contrast, in the homochalcogen complexes $[ReX(CO)_3\{o\text{-}MeS(C_6H_4)SMe\}]$ increasing the size of the halogen favoured the less sterically hindered *meso*-2 at the expense of *meso*-1 and DL isomers. These changes, however, did not affect the order of populations, namely *meso*-2 > DL-1 = DL-2 > *meso*-1, which applied throughout. This ordering was the exact reverse of that found for the isoelectronic and isostructural trimethylplatinum(IV) halide complexes.[4] In the latter complexes the bulky nature of the methyl groups, as opposed to the very low steric demands of carbonyl groups, preferentially forces the SMe groups away from the $PtMe_3$ moiety, thus favouring the *meso*-1 species.

The chemical shift variation of the E-methyl signals with halogen is particularly striking (Figure 2). When X = Cl, the four lowest-frequency signals D, C, B, and A due to the Se-methyls are quite separate from the S-methyl signals F, G, H, and E. For the complexes where X = Br or I the absorption regions of the two types of chalcogen methyls overlap considerably but can be rationalised as follows. The shifts associated with the methyls *trans* to the halogen X, namely methyls D, C, F, and G, are essentially unaffected by the halogen type, whereas the signals due to the methyls *cis* to X,

Table 2. Static parameters used in the calculation of pyramidal inversion energies for the complexes [ReX(CO)$_3${*o*-MeE(C_6H_4)E′Me}]

Complex				[*meso*-1] [a]/[DL-1] [b]		[DL-1]/[DL-2]		[DL-2]/[DL-4]		[*meso*-2]/[DL-3]		
X	E	E′	θ_c/°C	ν [c]	*p* [d]	ν	*p*	ν	*p*	ν	*p*	T_2^*/s
Cl	S	S	−59.0	310.2	0.255	294.1	0.215	305.1	0.215	308.3	0.315	0.191
	S			312.4		294.4		306.0		307.7		0.164
Cl			−63.9		0.116		0.201		0.273		0.410	
		Se		288.8		282.0		267.9		281.0		0.164
Br	S	S	−58.4	318.5	0.088	293.2	0.198	312.7	0.198	308.0	0.515	0.106
	S			320.5		293.8		316.6		307.0		0.143
Br			−64.5		0.046		0.160		0.242		0.552	
		Se		298.3		291.5		267.1		281.3		0.169
I	S	S	−53.8	329.8	0.023	293.5	0.152	324.8	0.152	308.0	0.673	0.218
	S			331.3		294.7	·	327.3		307.1		0.164
I			−63.9		0.016		0.108		0.138		0.738	
		Se		311.8		305.4		267.7		281.5		0.164

[a] Nomenclature for dithioether complexes. [b] Nomenclature for mixed-chalcogen ligand complexes. [c] Chemical shift (ν_i/Hz) of E-methyls measured relative to $SiMe_4$ at 100 MHz. [d] Isomer population.

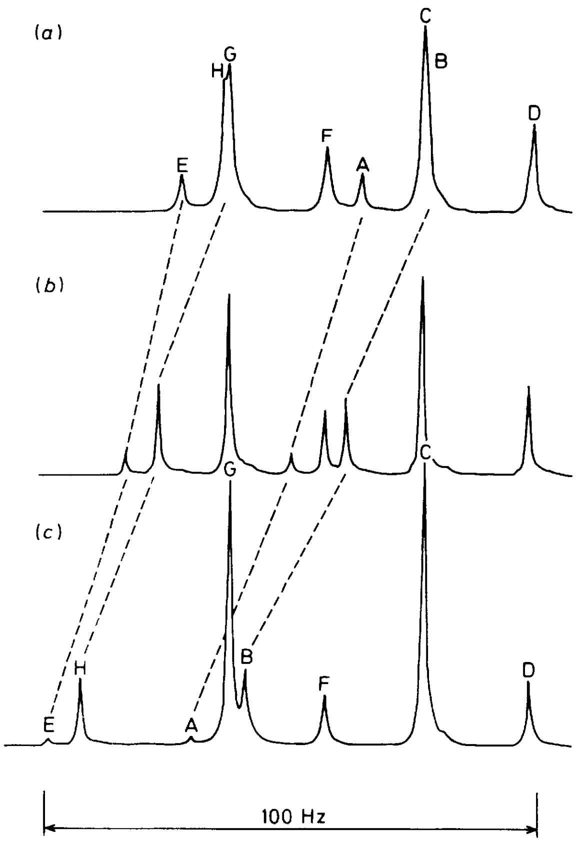


Figure 2. 400-MHz ^{1}H N.m.r. spectra of the ligand-methyl region for [ReX(CO)$_3${*o*-MeS(C_6H_4)SeMe}] [X = Cl (*a*), Br (*b*), or I (*c*)] at low temperatures (*ca.* −70 °C) showing the halogen dependence of chemical shifts and invertomer populations. Lines are labelled according to Figure 1, namely A,E [DL-1], B,F [DL-2], C,G [DL-3], and D,H [DL-4]

namely B, A, H, and E, are moved steadily to higher frequencies as the halogen electronegativity decreases.

$$A \underset{}{\overset{k_{12}^S}{\rightleftharpoons}} B \text{ and } E \overset{k_{12}^S}{\rightleftharpoons} F \quad (\text{DL-1} \rightleftharpoons \text{DL-2})$$

$$D \underset{k_{34}^S}{\rightleftharpoons} C \text{ and } H \underset{k_{34}^S}{\rightleftharpoons} G \quad (\text{DL-4} \rightleftharpoons \text{DL-3})$$

Scheme 1.

With increasing solvent temperature the spectra of [ReX(CO)$_3${*o*-MeE(C_6H_4)E′Me}] complexes in solution showed evidence of pyramidal inversion of the E atoms. In the homochalcogen complexes (E = E′ = S) the energy of the inversion process was measured in exactly the same way as for the saturated and unsaturated thio- and seleno-ether complexes.[1] The resulting Arrhenius and Eyring energy data are reported in Table 3. For the heterochalcogen complexes (E = S, E′ = Se) the S and Se inversions are assumed to be essentially independent processes and interconvert the four DL species according to the scheme in Figure 1. Such a scheme has been discussed earlier for the trimethylplatinum(IV) complexes[4] and so will only be summarised here. Four sulphur rate constants and four selenium rate constants are required fully to characterise the process. However, the two types of rate constants have different orders of magnitude since in the temperature range −70 to 35 °C for the complex with X = Br only sulphur inversion occurred, the effect of selenium inversion only being apparent in the range 50—120 °C. The spectral changes for [ReBr(CO)$_3${*o*-MeS(C_6H_4)-SeMe}] in these two temperature ranges are depicted in Figures 3 and 4. In the low-temperature range the eight signals coalesce in pairs to four signals according to the dynamic spin problem in Scheme 1. Excellent fits between experimental and computer-synthesised spectra were obtained as shown in Figure 3, where for each temperature the ' best fit ' rate constants for sulphur inversion are shown. Barrier energies for the two sulphur-inversion pathways were computed in the usual way.[4] At ambient temperatures when sulphur inversion is rapid, the four signals, due to the averaged chemical shifts ⟨AB⟩, ⟨CD⟩, ⟨EF⟩, and ⟨GH⟩, were relabelled L, P, M, and N respectively, and assigned according to Figure 5. These assignments were based on the observation of ^{77}Se satellites for lines L and P, and on the chemical shift variation of line P with halogen, which indicated that it was due to a methyl *cis* to the halogen (see above). Subsequent selenium inversion interconverted the DL-1/2 and DL-3/4 species according to Scheme 2.

The spectra in Figure 4 show that this process becomes rapid for X = Br at *ca.* 120 °C, when two relatively sharp lines are observed. These spectral changes were again computed in the standard way, the spin problem being of the type in Scheme 3.

This approach provides a single energy barrier to selenium inversion. It is of theoretical interest to note that if the rates of

Table 3. Arrhenius and Eyring activation parameters for sulphur and selenium inversion in complexes of the type [ReX(CO)$_3$(L–L)]

Complex							
X	L–L	Inversion	E_a/kJ mol^{-1}	$\log_{10}A$	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta G^{\ddagger\,a}$/kJ mol^{-1}
Cl	o-MeSC$_6$H$_4$SMe	S$_1$ [b]	57.9 ± 0.1	13.2 ± 0.02	1.1 ± 0.5	55.8 ± 0.1	55.5 ± 0.1
		S$_2$ [c]	57.9 ± 1.2	13.4 ± 0.2	5.1 ± 4.8	55.8 ± 1.2	54.3 ± 0.2
Br	o-MeSC$_6$H$_4$SMe	S$_1$	56.2 ± 1.0	13.0 ± 0.2	−2.7 ± 3.8	54.1 ± 0.9	54.9 ± 0.2
		S$_2$	55.6 ± 1.2	13.1 ± 0.2	−0.1 ± 4.6	53.5 ± 1.1	53.5 ± 0.2
I	o-MeSC$_6$H$_4$SMe	S$_1$	54.2 ± 1.2	12.4 ± 0.2	−14.7 ± 4.7	52.0 ± 1.2	56.4 ± 0.2
		S$_2$	52.9 ± 1.4	12.4 ± 0.3	−15.2 ± 5.7	50.7 ± 1.5	55.3 ± 0.2
Br	o-MeSC$_6$H$_4$SeMe	S$_1$ [d]	51.4 ± 1.2	12.7 ± 0.2	−8.8 ± 4.6	49.2 ± 1.2	51.8 ± 0.1
		S$_2$ [e]	52.6 ± 1.1	12.8 ± 0.2	−7.6 ± 4.3	50.5 ± 1.1	52.8 ± 0.1
		Se [f]	84.9 ± 1.4	13.3 ± 0.2	−1.2 ± 3.7	81.9 ± 1.4	82.2 ± 0.3

[a] At 298.15 K. [b] [*meso*-1] $\longrightarrow$ [DL-1]. [c] [DL-1] $\longrightarrow$ [*meso*-2]. [d] [DL-1] $\longrightarrow$ [DL-2]. [e] [DL-3] $\longrightarrow$ [DL-4]. [f] [DL-1/2] $\longrightarrow$ [DL-3/4].

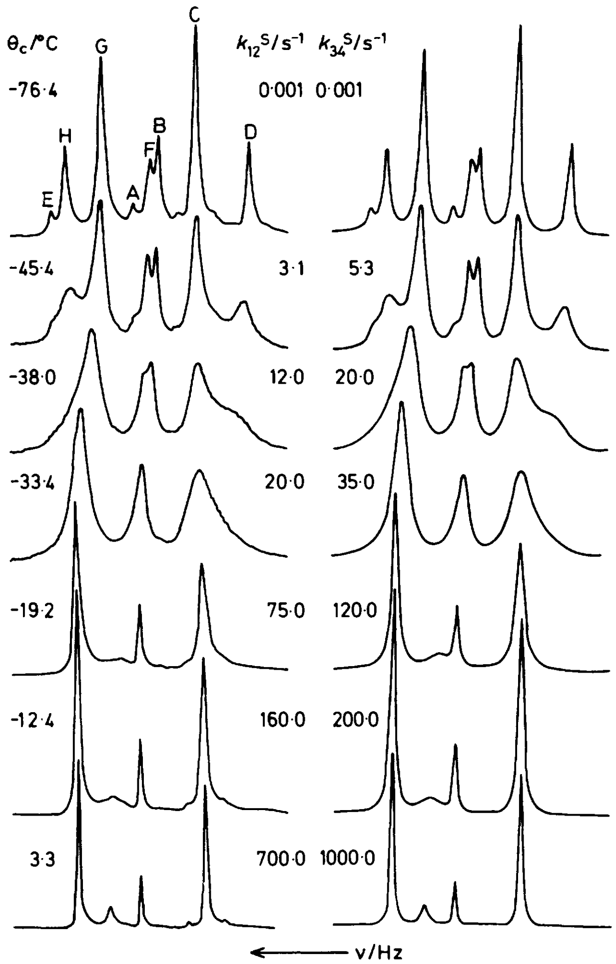


Figure 3. Experimental and computer-synthesised spectra of [ReBr(CO)$_3${o-MeS(C$_6$H$_4$)SeMe}] showing the effects of sulphur inversion

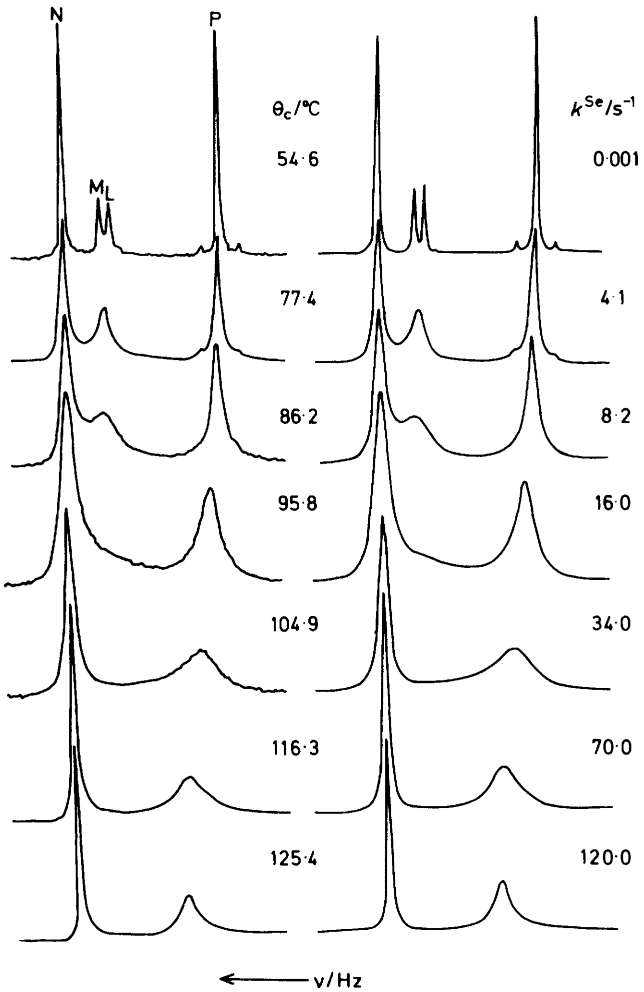


Figure 4. Experimental and computer-synthesised spectra of [ReBr(CO)$_3${o-MeS(C$_6$H$_4$)SeMe}] showing the effects of selenium inversion. See text for labelling

the sulphur and selenium inversions were similar, then *two* selenium inversion barriers in addition to the two sulphur barriers would have been calculable. In the present case, the single selenium barrier computed may be considered as an average of the barriers associated with the two theoretically distinct pathways. The static parameters for these mixed-chalcogen complexes are given in Table 4 and the activation energies for [ReBr(CO)$_3${o-MeS(C$_6$H$_4$)SeMe}] quoted in Table 3 alongside the energies for the dithio-ligand analogues.

Discussion

The activation-energy parameters given in Table 3 reveal a number of interesting trends which may be summarised as follows.

(*i*) The $\Delta G^\ddagger$ values for S inversion lie in the range 51—56 kJ mol^{-1} while the value for Se inversion is *ca.* 25 kJ mol^{-1} higher. A recent review [11] has shown that sulphur-inversion energies are invariably lower than selenium-inversion energies

Table 4. Static parameters for calculating the selenium-inversion barrier in the heterochalocogen complexes [ReX(CO)$_3${*o*-MeSC$_6$H$_4$SeMe}]

Complex	θ_c [a]/ °C	Sulphur methyls					Selenium methyls						
		ν_M [b]	p_M [c]	ν_N	p_N [d]	T_2^*/s	ν_L	^2J [e]	p_L [c]	ν_P	^2J	p_P [d]	T_2^*/s
[ReCl(CO)$_3${*o*-MeSC$_6$H$_4$SeMe}]	43.3	297.0	32.0	302.4	68.0	0.409	280.4	10.1	32.0	270.6	9.9	68.0	0.458
[ReBr(CO)$_3${*o*-MeSC$_6$H$_4$SeMe}]	46.3	298.7	20.5	306.1	79.5	0.395	289.3	10.5	20.5	271.1	9.9	79.5	0.470
	54.6 [f]	270.9	21.0	280.8	79.0	0.382	238.9	10.0	21.0	268.3	9.9	79.0	0.458
[ReI(CO)$_3${*o*-MeSC$_6$H$_4$SeMe}]	43.3	299.9	13.5	309.6	86.5	0.382	303.1	10.3	13.5	272.6	10.4	86.5	0.410

[a] Solvent was CD$_2$Cl$_2$ except where stated otherwise. [b] Chemical shift (ν_i/Hz) of E-methyls relative to SiMe$_4$. [c] Population (%) of (DL-1 + DL-2) invertomers. [d] Population (%) of (DL-3 + DL-4) invertomers. [e] $^2J(^{77}$Se–C–^{1}H)/Hz. [f] Solvent C$_6$D$_5$NO$_2$–C$_6$D$_6$.

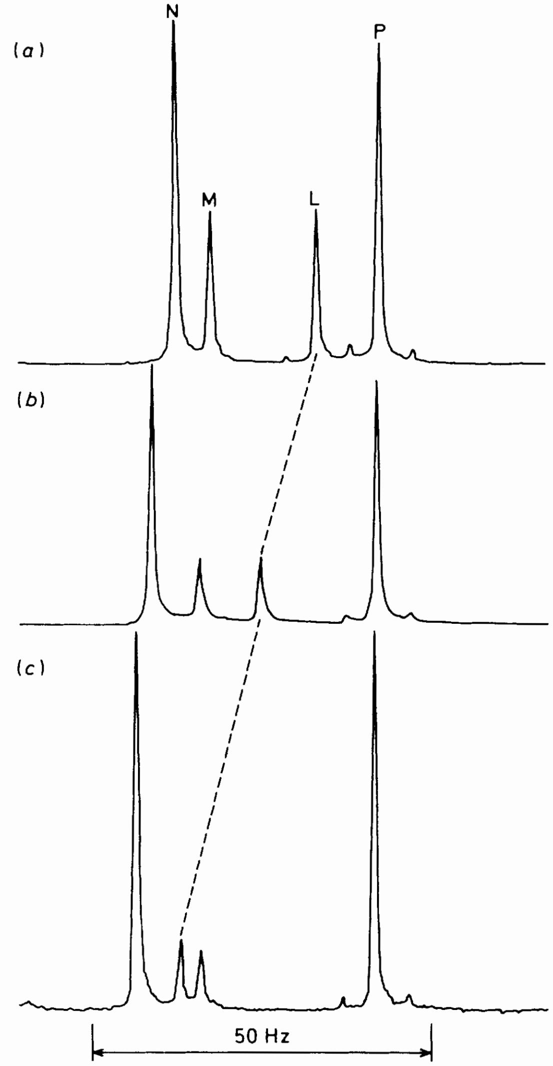
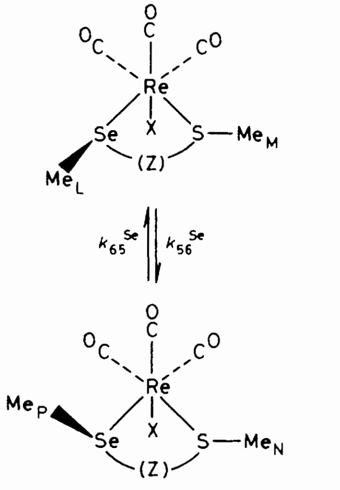


Figure 5. 100-MHz ^{1}H n.m.r. spectra of [ReX(CO)$_3${*o*-MeSe(C$_6$H$_4$)-SMe}] [X = Cl (*a*), Br (*b*), or I (*c*)] in CD$_2$Cl$_2$ at *ca.* 46 °C showing the halogen dependence of the methyl signals in the limit of fast sulphur inversion and slow selenium inversion. See text for line labelling

when closely analogous compounds are compared. However, the difference in $\Delta G^\ddagger$ values ($\Delta\Delta G^\ddagger$Se/S) varies considerably in magnitude (*e.g.* the range is 8—22 kJ mol^{-1} for a variety of complexes of Re^{I}, Pd^{II}, Pt^{II}, and Pt^{IV}). In the present rhenium(I) complexes the difference between S and Se inversion barriers is therefore exceptionally high.

(*ii*) A comparison of the above $\Delta G^\ddagger$ data with those obtained for the isostructural trimethylplatinum(IV) halide complexes [4] shows that the S inversion barriers are 4—5 kJ mol^{-1} higher, and the Se barriers 12—15 kJ mol^{-1} higher in the rhenium(I) complexes. This probably reflects a greater stabilisation of the transition state in the platinum(IV) complexes as a result of the electronegativity of the metal and/or the effect of (p–d)π conjugation between the chalcogen and the metal.



DL-1/2 (5)

DL-3/4 (6)

Scheme 2.

$$\mathrm{L} \underset{}{\overset{k^{\mathrm{Se}}}{\rightleftharpoons}} \mathrm{P} + \mathrm{LY} \overset{k^{\mathrm{Se}}}{\rightleftharpoons} \mathrm{PY} \qquad \mathrm{Y} = {}^{77}\mathrm{Se}$$

$$(92.4\%) \qquad\qquad (7.6\%)$$

$$\text{and } \mathrm{M} \overset{k^{\mathrm{Se}}}{\rightleftharpoons} \mathrm{N}$$

Scheme 3.

(*iii*) The $\Delta G^\ddagger$ data in Table 3 show no obvious dependence on the nature of the halogen, in line with usually negligible *cis*-halogen influences. A well defined *cis* influence has been identified only in the case of some palladium(II) complexes.[12]

(*iv*) A comparison of the data in Table 3 with data for the corresponding aliphatic and olefinic ligand complexes [1] allows the dependence of chalcogen-inversion energies on the type of ligand backbone to be deduced. Replacement of a saturated aliphatic backbone, –CH$_2$CH$_2$–, by an aromatic moiety, *o*-C$_6$H$_4$, lowers the $\Delta G^\ddagger$ values for sulphur and selenium inversion by *ca.* 9—10 and *ca.* 6—7 kJ mol^{-1} respectively; furthermore, the change from aromatic to olefinic, –CH=CH–, backbone causes an additional lowering of 1—2 kJ mol^{-1}. This is almost certainly the result of (p–p)π conjugation between the chalcogen lone pair and ligand backbone which is more effective in the planar transition state than in the pyramidal ground state. Similar trends have been noted in palladium(II),[5] platinum(II),[5] and platinum(IV) [3,4,13] complexes. Conjugation effects have also been noted in cases of inverting Group 5B atoms such as phosphorus and arsenic.[14-16]

(*v*) No fluxional processes other than chalcogen inversions were observed in these rhenium(I) complexes. In the analogous trimethylplatinum(IV) halide complexes, however, rapid inversions at both chalcogen sites were followed by 180° ligand rotations about the Pt^{IV} atom. The highly non-rigid intermediate associated with this novel fluxion initiated scrambling of the platinum-methyl environments. The detection of similar ligand rotations leading to scrambling of the rhenium-carbonyl environments in these rhenium(I) complexes is far more difficult. It is necessary to detect the coalescence of the carbonyl-carbon signals in the ^{13}C n.m.r. spectra, but it has not proved possible to date to obtain sufficiently intense spectra owing to the limited amounts of material available and the moderate solubilities of these complexes in suitable high-temperature n.m.r. solvents. The possible occurrence of high-temperature fluxions in these rhenium(I) complexes must remain an open question at present. If such fluxions can be identified the same type of graph diagram used for describing the stereodynamics of the trimethylplatinum(IV) complexes [4] will be valid here. At present, the four edges (pathways) connecting the front and back faces of the cube are yet to be established.

Acknowledgements

We thank the S.E.R.C. for use of the 400-MHz ^1H n.m.r. facilities at the University of Warwick.

References

1 E. W. Abel, S. K. Bhargava, M. M. Bhatti, K. Kite, M. A. Mazid, K. G. Orrell, V. Šik, B. L. Williams, M. B. Hursthouse, and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1982, 2065.
2 E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Šik, *J. Chem. Soc., Dalton Trans.*, 1980, 1169.
3 E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Šik, *J. Chem. Soc., Dalton Trans.*, 1980, 1175.
4 E. W. Abel, S. K. Bhargava, K. Kite, K. G. Orrell, V. Šik, and B. L. Williams, *J. Chem. Soc., Dalton Trans.*, 1982, 583.
5 E. W. Abel, S. K. Bhargava, K. Kite, K. G. Orrell, V. Šik, and B. L. Williams, *Polyhedron*, 1982, 289.
6 E. W. Abel, K. Kite, K. G. Orrell, V. Šik, and B. L. Williams, *J. Chem. Soc., Dalton Trans.*, 1981, 2439.
7 S. E. Livingstone, *J. Chem. Soc.*, 1956, 437.
8 C. G. Pierpont, B. J. Corden, and R. Eisenberg, *Chem. Commun.*, 1969, 401.
9 G. Binsch and H. Kessler, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 411.
10 E. W. Abel and S. P. Tyfield, *Can. J. Chem.*, 1969, **47**, 4627.
11 E. W. Abel, S. K. Bhargava, and K. G. Orrell, *Prog. Inorg. Chem.*, in the press.
12 E. W. Abel, M. Booth, and K. G. Orrell, *J. Chem. Soc., Dalton Trans.*, 1979, 1994.
13 E. W. Abel, S. K. Bhargava, K. G. Orrell, A. W. G. Platt, V. Šik, and T. S. Cameron, unpublished work.
14 A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 400.
15 W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, 1971, **93**, 6205.
16 R. H. Bowman and K. Mislow, *J. Am. Chem. Soc.*, 1972, **94**, 2861.

Received 1*st June* 1983; *Paper* 3/893