Dynamic Nuclear Magnetic Resonance Study of Group 6 Metal Pentacarbonyl Complexes. Pyramidal Inversion and 1,2-Metal Shifts in the Complexes $[\mathrm{M(CO)_5(Me_2\overline{CCH_2EEC}H_2)}]$ (M = Cr, Mo, or W; E = S or Se)†

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Mononuclear complexes of the type $[\mathrm{M(CO)_5(Me_2\overline{CCH_2EEC}H_2)}]$, where M = Cr, Mo, or W and E = S or Se, have been prepared. Detailed variable-temperature n.m.r. studies have established the existence of pyramidal inversion about the co-ordinated sulphur or selenium ligand atom and an intramolecular 1,2-metal shift between adjacent chalcogen ligand atoms. The energy barriers associated with both rate processes have been evaluated by dynamic n.m.r. methods. The metal pentacarbonyl complexes of naphtho[1,8-*cd*]-dithiole and -thiaselenole, $[\mathrm{M(CO)_5(C_{10}H_6EE')}]$ (M = W, E = E′ = S; M = Cr, E = S, E′ = Se) have also been prepared but no fluxionality was evident.

In recent years we have identified a wide range of complexes exhibiting fluxional phenomena.[1–7] In particular, complexes with sulphur- and/or selenium-containing ligands have been shown to undergo intramolecular rearrangements such as pyramidal atomic inversion, six-membered ligand ring reversal,[2–5] 1,2-metal shifts,[6] and 1,3-metal shifts.[7] The energy barriers for these fluxions have been described previously,[2–7] by utilising well developed n.m.r. band-shape analysis techniques.[8]

We have already briefly reported the effects of pyramidal atomic inversion and 1,2-metal shifts in Group 6 metal pentacarbonyl complexes with acyclic disulphides and diselenides.[6] In the case of the five-membered cyclic disulphides and diselenides reported herein the energy barriers for the above mentioned fluxions are substantially different from those of their acyclic ligand analogues. Proton n.m.r. spectra between −80 and 120 °C reveal pyramidal atomic inversion about the co-ordinated ligand sulphur or selenium atoms, while at temperatures well above those where inversion is fast a rapid intramolecular commutation of the $\mathrm{M(CO)_5}$ moiety over both chalcogen atom co-ordination sites occurs. Arrhenius and Eyring activation parameters have been evaluated and $\Delta G^{\ddagger}$ values, calculated at a standard temperature (298.15 K), reveal a number of interesting features.

Experimental

All reactions described below were carried out under an atmosphere of dry nitrogen, using solvents which were either sodium-dried or distilled from potassium–benzophenone.

All complexes with one exception were made by an established procedure,[9] in which pentacarbonylhalogenometalates[10] of Group 6 react with ligands, L, in the presence of a Lewis acid to give $[\mathrm{M(CO)_5L}]$ (M = Cr, Mo, or W) complexes. The starting materials were prepared by well described literature methods.

The preparation of the ligand 4,4-dimethyl-1,2-diselenacyclopentane, based on a modified version of the synthesis of 2,3-diselenaspiro[4.5]decane[11] was as follows. The reaction was carried out by a slow addition of 1,3-dibromo-2,2-dimethylpropane (0.05 mol) to KSeCN (0.1 mol) dissolved in $\mathrm{O(CH_2CH_2OH)_2}$ (*ca.* 200 cm^3). Heating at 140—150 °C for 2 h and at *ca.* 200 °C for 20 h produced a dark red-brown solution, which was extracted with light petroleum (b.p. 80—100 °C), washed with water, and dried over $\mathrm{CaCl_2}$ for *ca.* 4 h. After distilling off the solvent, a viscous liquid resulted, to which was added some absolute alcohol. Brown needles were obtained after recrystallisation, m.p. 34 °C (lit.,[12] 34 °C). ^{1}H N.m.r. (in $\mathrm{CD_2Cl_2}$–$\mathrm{CS_2}$ or $\mathrm{CDCl_3}$): δ 1.27 (Me) and 3.08 p.p.m. ($\mathrm{CH_2}$).

The 4,4-dimethyl-1,2-dithiacyclopentane ligand was prepared according to the above method but using KSCN. B.p. 90—92 °C (20 mmHg) [lit.,[13] 84—86 °C (17 mmHg)]. ^{1}H N.m.r. (in $\mathrm{CD_2Cl_2}$–$\mathrm{CS_2}$ or $\mathrm{CDCl_3}$): δ 1.26 (Me) and 2.88 p.p.m. ($\mathrm{CH_2}$).

The ligands naphtho[1,8-*cd*]dithiole ($\mathrm{C_{10}H_6S_2}$) and naphtho[1,8-*cd*]thiaselenole ($\mathrm{C_{10}H_6SSe}$) were prepared by the method of Meinwald *et al.*[14] using 8-chloro-1-naphthalenethiol[15] as precursor. The tungsten(0) complex $[\mathrm{W(CO)_5(C_{10}H_6S_2)}]$ was synthesised by the action of the ligand on the pentacarbonyl(tetrahydrofuran)tungsten precursor,[16] while $[\mathrm{Cr(CO)_5(C_{10}H_6SSe)}]$ was isolated by the method described above[9] for the other five-membered ligand ring complexes.

The ^{1}H n.m.r. spectra were recorded using a JEOL-PFT-100 spectrometer with a standard JES-VT-3 unit to control the temperature. Temperature measurements, using a precisely calibrated thermocouple, were made immediately before and after recording the spectra, and are accurate to at least ±1 °C. Microanalyses were performed by Butterworth Laboratories Ltd., London. Melting points (uncorrected) were determined using an Electrothermal apparatus.

Results and Discussion

The complexes, prepared as described above, are crystalline solids readily soluble in organic solvents but unstable both in air and, particularly, in solution. The stabilities of the complexes, both in the solid state and in solution, followed the trends W > Cr > Mo and Se > S. Analytical data are reported in Table 1. All i.r. data for carbonyl-stretching absorptions were obtained in n-hexane solutions, and consist of four bands one of which is due to a small amount of metal hexacarbonyl[17] (*ca.* 1 983—1 990 cm^{-1}) (Table 1).

The six complexes $[\mathrm{M(CO)_5(Me_2\overline{CCH_2EEC}H_2)}]$ (M = Cr, Mo, or W; E = S or Se) showed gross n.m.r. spectral changes in the range of −25 to 120 °C for selenium-containing ligands and in the range −80 to 110 °C for their sulphur analogues. In contrast, the spectra of the complexes $[\mathrm{M(CO)_5(C_{10}H_6EE')}]$ were invariant with temperature up to the points at which irreversible decomposition occurred. These complexes were characterised by elemental analyses and/or their ^{13}C n.m.r. data. Details of the latter (for both free ligands[18] and complexes) are given in Table 2. Full assignments could not be

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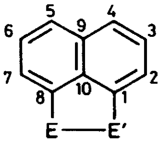
† *Non-S.I. unit employed:* mmHg ≈ 133 Pa.

Table 1. Characterisation of the mononuclear complexes (d.p. = decomposition point)

Complex	Colour	D.p./°C	Elemental analysis[a] (%) C	H	I.r. (carbonyl) bands[b] (cm^{-1})
$[Cr(CO)_5(Me_2CCH_2SSCH_2)]$	Orange	64—66	37.4 (36.8)	3.1 (3.1)	2 071w, 1 987vw, 1 951s, 1 940m
$[Mo(CO)_5(Me_2CCH_2SSCH_2)]$	Greenish pale yellow	52—53	32.45 (32.45)	2.8 (2.7)	2 079w, 1 989w, 1 953s, 1 937m
$[W(CO)_5(Me_2CCH_2SSCH_2)]$	Pale yellow	68—69	26.25 (26.2)	2.2 (2.2)	2 076w, 1 984vw, 1 948s, 1 937m
$[Cr(CO)_5(Me_2CCH_2SeSeCH_2)]$	Dark red-brown	97—98	28.5 (28.6)	2.35 (2.4)	2 069w, 1 988vw, 1 952s, 1 944(sh)
$[Mo(CO)_5(Me_2CCH_2SeSeCH_2)]$	Dark red	87	25.8 (25.9)	2.05 (2.15)	2 079w, 1 983vw, 1 954s, 1 942m
$[W(CO)_5(Me_2CCH_2SeSeCH_2)]$	Brown	102—104	21.85 (21.75)	1.85 (1.85)	2 073w, 1 985vw, 1 949s, 1 940(sh)
$[W(CO)_5(C_{10}H_6S_2)]$	Dark red-brown	120—122	*c*	*c*	2 076w, 1 983m, 1 960m, 1 949m
$[Cr(CO)_5(C_{10}H_6SSe)]$	Brown	110	43.55 (41.95)	1.35 (1.4)	2 070w, 1 989vw, 1 957s, 1 951 (sh), 1 945m

[a] Calculated values in parentheses. [b] Recorded in n-hexane; spectra calibrated against polystyrene film. The bands in the range 1 983—1 990 cm^{-1} are due to trace amounts of $[M(CO)_6]$. [c] Not determined.

Table 2. ^{13}C N.m.r. data for the complexes $[M(CO)_5L]$



L

<table>
<tr><th>E</th><th>E′</th><th>M</th><th>$C^{2,7}$</th><th>$C^{3,6}$</th><th>$C^{4,5}$</th><th>C^9</th><th>C^{10}</th><th>$C^{1,8}$</th></tr>
<tr><td>S</td><td>S</td><td></td><td>115.86</td><td>127.82</td><td>121.56</td><td>134.68</td><td>135.63</td><td>144.00</td></tr>
<tr><td>Se</td><td>Se</td><td></td><td>121.12[a]</td><td>127.62[a]</td><td>123.75[a]</td><td>137.50[a]</td><td>137.89[a]</td><td>140.91[a]</td></tr>
<tr><td>S</td><td>Se</td><td></td><td>118.21,
119.23</td><td>127.43,
127.67</td><td>122.14,
123.26</td><td>136.04</td><td>136.60</td><td>140.51,[b]
144.49[c]</td></tr>
<tr><td>S</td><td>S</td><td>W[d]</td><td colspan="3">118.33, 123.70, 127.72
120.44, 126.41, 128.49</td><td colspan="3">134.88, 152.69, 166.55
172.06</td></tr>
<tr><td>S</td><td>Se</td><td>Cr[d]</td><td colspan="3">120.22, 123.89, 127.80
123.06, 127.41, 128.14</td><td colspan="3">135.90[e]</td></tr>
</table>

[a] Shift value from ref. 18. Assignment not previously given. [b] C^1–Se. [c] C^8–S. [d] Shift data of metal complexes are given in increasing magnitude and no definite carbon assignments are implied. [e] Remaining signals too weak to be detected.

made, nor was it possible to deduce whether co-ordination in the chromium(0) complex was to sulphur or selenium. However, the ^{13}C spectrum indicated a *single* complex species and, by analogy with the structures of $[M(CO)_5(MeSCH_2SeMe)]$,[7] is attributed to the selenium-bonded complex.

The variable-temperature studies of the complexes $[M(CO)_5(Me_2CCH_2EECH_2)]$ will now be exemplified by the complex (M = W, E = S).

Low-temperature ^1H *N.M.R. Studies.*—The spectrum of the complex $[W(CO)_5(Me_2CCH_2SSCH_2)]$ at room temperature, consisting of two singlets of equal intensity and another of higher intensity, indicates that the complex is already undergoing rapid sulphur inversion. The two singlets of intensity ratio 1 : 1 are assigned to the two methylene groups and the other signal to both methyl groups. On cooling to −70 °C, each methylene group appears as an AB quartet (Figure 1) and the methyl-group signal resolves into two. The assignment of the methylene AB quartets was straightforward, that with the larger chemical-shift difference being due to the CH_2 group *adjacent* to the co-ordinated sulphur atom. This spectrum is consistent with a 'static' ligand structure, *i.e.* one with no pyramidal atomic inversion of the co-ordinated sulphur atom. The effect of the inversion process is shown in Scheme 1 by the horizontal interconversions. The methylene hydrogens are labelled as H_A,H_B and H_C,H_D according to whether they are attached to the co-ordinated or unco-ordinated sulphur atom. These spectral changes were accurately studied in the approximate range −70 to −20 °C.

High-temperature ^1H *N.M.R. Studies.*—At temperatures well above those where S/Se inversion was fast on the n.m.r. time-scale, all the complexes, except $[Mo(CO)_5(Me_2CCH_2SeSeCH_2)]$ were observed to undergo an additional exchange process. The spectral changes, studied in the approximate range 20—120 °C, imply a rapid intramolecular commutation of the $M(CO)_5$

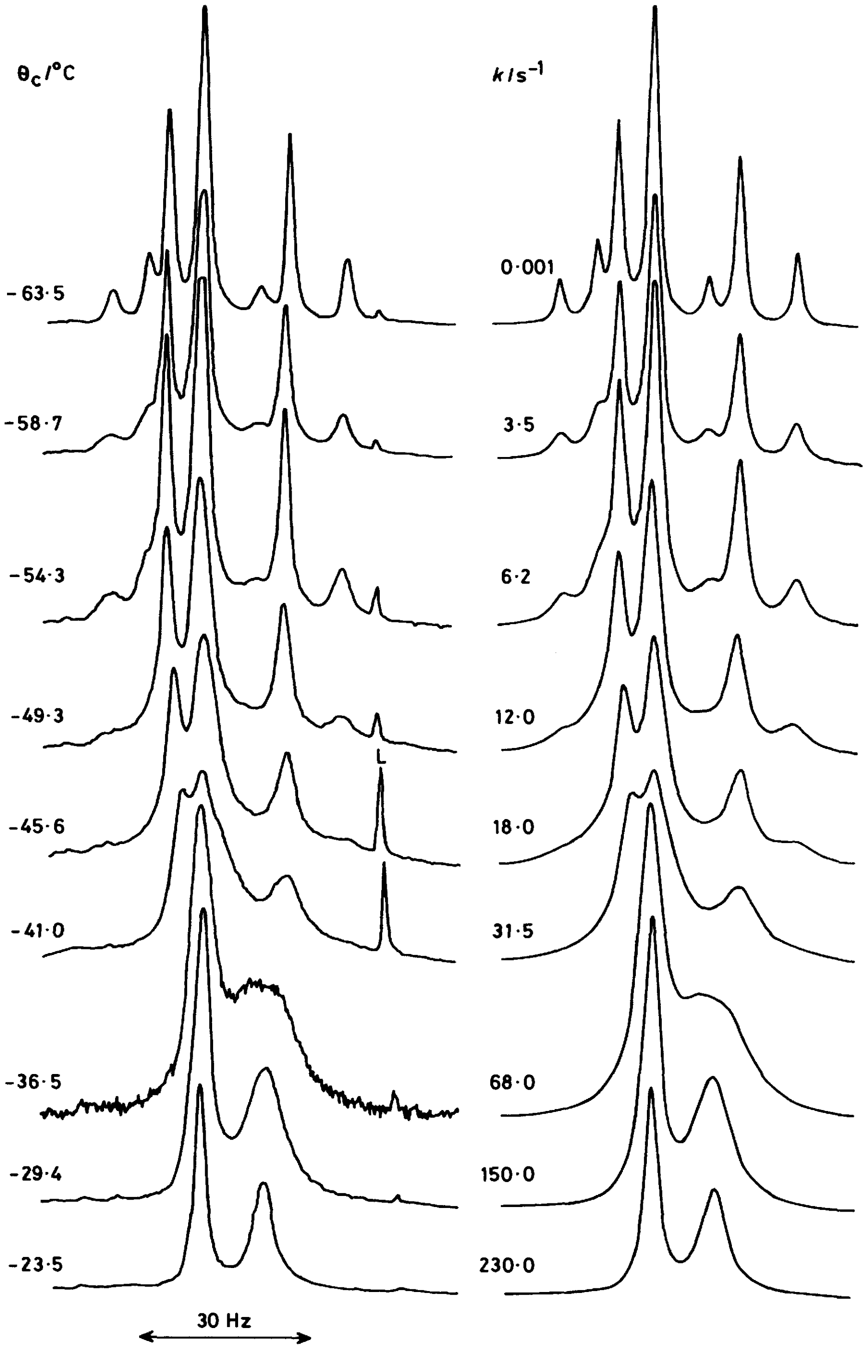


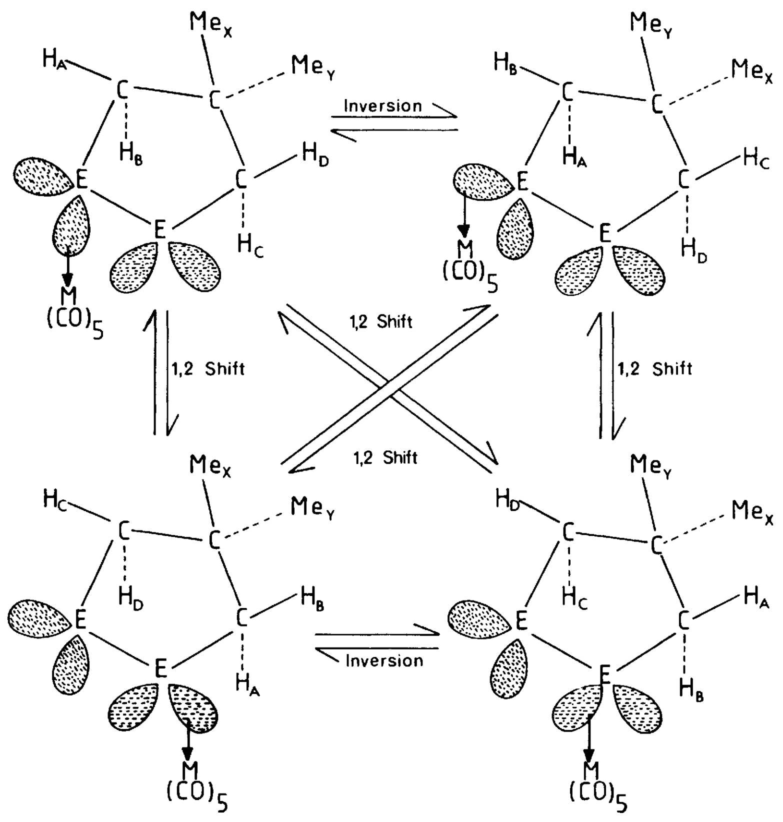
Figure 1. Experimental and computer-simulated low-temperature spectra of the methylene region of the complex $[\mathrm{W(CO)_5(Me_2\overline{CCH_2SSCH_2})}]$, showing the effect of pyramidal sulphur inversion; L refers to free ligand

moiety over both chalcogen atom co-ordination sites *via* a 1,2-shift process. Taking the example of the S-ligand chromium complex, the two different methylene signals were apparent at room temperature. On increasing the temperature to *ca.* 95 °C these two singlets collapsed to a single band which sharpened on further elevation of temperature, clearly indicating the rapid 1,2 shift of the metal pentacarbonyl moiety. The intramolecular nature of the fluxion is confirmed by a complete absence of exchange with added free ligand over the entire range of temperature. The process is represented by the vertical and diagonal changes in Scheme 1 and illustrated in Figure 2.

The static parameters, namely chemical shifts, spin-coupling constants $^2J(\mathrm{HH})$ and the effective proton transverse-relaxation times T_2^*, used in the band-shape fittings are given in Tables 3 and 4.

In order accurately to fit the experimental band shapes, the temperature dependence of the methylene chemical-shift differences had to be assessed. Chemical-shift differences were obviously only directly measurable at very slow rates of inversion. Values used for the band-shape fittings were based on linear extrapolations of the low-temperature values.

The sets of experimental and computer-synthesised spectra for sulphur inversion and 1,2-metal shift are shown in Figures 1 and 2 respectively. The total dynamic spin problem for the



Scheme 1. The effect of sulphur inversion and 1,2-metal shift on the environments of the methylene protons

Table 3. Static parameters for calculating the pyramidal inversion energies in complexes of type $[M(CO)_5(Me_2CCH_2EECH_2)]$

Complex				–CH$_2$–						
M	E	θ_c/°C	Solvent	ν_A/Hz	ν_B/Hz	ν_C/Hz	ν_D/Hz	^2J(AB)/ Hz	^2J(CD)/ Hz	T_2^*/s
Cr	Se	−2.7	C_2Cl_4–C_6D_6 [a]	300.9	242.5	289.2	266.1	10.3	10.3	0.153
Mo	Se	−23.2	$CDCl_3$ [a]	352.5	317.4	341.8	329.8	10.4	10.4	0.153
W	Se	−2.7	C_2Cl_4–C_6D_6 [a]	323.1	268.4	312.0	286.9	10.3	10.3	0.183
Cr	S	−66.3	CD_2Cl_2 [b]	330.4	309.0	328.7	304.9	11.25	10.75	0.143
Mo	S	−79.6	CD_2Cl_2 [b]	331.1	309.8	338.1	314.2	11.0	11.2	0.143
W	S	−63.5	$CDCl_3$ [b]	333.4	308.7	339.7	326.3	11.0	11.0	0.163

[a] Reference material, hexamethyldisiloxane (hmds). [b] Reference material, $SiMe_4$.

Table 4. Static parameters used in the calculation of the 1,2-shift energies for the complexes $[M(CO)_5L]$

			–CH$_2$– Shifts[a]/Hz		
M	L	θ_c/°C	⟨AB⟩	⟨CD⟩	T_2^*/s
Cr	$Me_2CCH_2SSCH_2$	49.5	256.0	244.5	0.254
Mo	$Me_2CCH_2SSCH_2$	23.0	266.1	255.4	0.127
W	$Me_2CCH_2SSCH_2$	60.5	282.7	262.2	0.208
Cr	$Me_2CCH_2SeSeCH_2$	50.1	274.4[b]	282.4[b]	0.153
W	$Me_2CCH_2SeSeCH_2$	57.6	297.6[b]	305.0[b]	0.183

[a] Chemical shifts are relative to hmds. Solvent was C_2Cl_4–C_6D_6 (75:25). [b] Not measured directly from the spectra but based on appropriate temperature extrapolations and averagings of the static chemical shifts (see Table 2).

methylene protons is represented in Scheme 2. However, since the rate of 1,2-metal shift only becomes significant after the inversion process has become rapid, the two rate processes are totally separable and the n.m.r. band-shape changes can be fitted as $ABCD \rightleftharpoons BADC$ and $\langle AB\rangle \rightleftharpoons \langle CD\rangle$ spin problems.

The Arrhenius and Eyring activation parameters for the pyramidal inversion and 1,2-metal shift fluxions are shown in Tables 5 and 6. It has been well established[8] that the $\Delta G^\ddagger$ parameter is least sensitive to systematic errors in temperature and rate constant, so discussions of the relative ease of the fluxional processes are based upon the $\Delta G^\ddagger$ (298.15 K) values listed in Tables 5 and 6.

Pyramidal Inversion.—The activation parameters associated with the Eyring equation presented in Table 5 reveal the dependences of the inversion energy ($\Delta G^\ddagger$) upon the inverting atom and metal centre. Thus, $\Delta G^\ddagger$ in the tungsten complex is *ca.* 1.5 kJ mol^{-1} higher than the value observed in its chromium analogue, which in turn is higher than the value in the molybdenum complex by *ca.* 6 kJ mol^{-1}. This is an expected trend and consistent with previous observations on Group 6 metal pentacarbonyl complexes.[19–22] Such a trend is thought to be a result

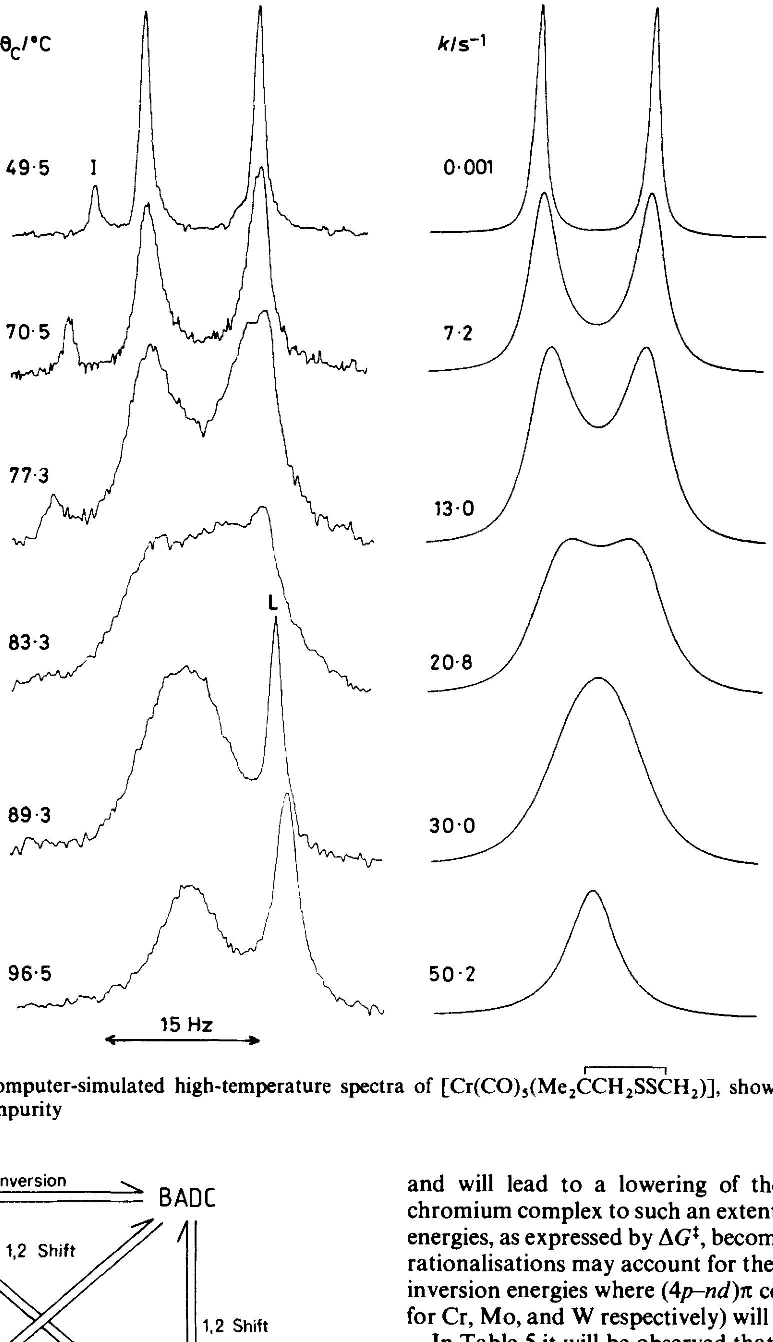
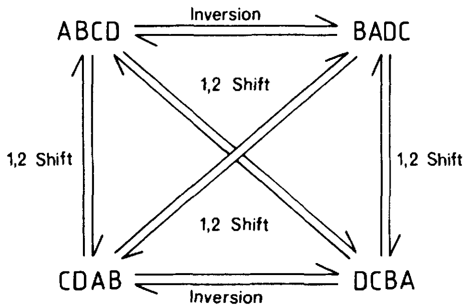


Figure 2. Experimental and computer-simulated high-temperature spectra of $[\mathrm{Cr(CO)_5(Me_2\overline{CCH_2SSCH_2})}]$, showing the effect of the 1,2-shift process; L = free ligand, I = impurity



Scheme 2. The spin problem for inversion and 1,2 shift

of two main factors, *i.e.*, the electronegativities of the metals and $(p\text{–}d)\pi$ conjugation of lone pairs of electrons on the inverting sulphur/selenium atom with the metal.[23,24] The electronegativities of the metals are in the order Cr > W > Mo,[25–27] so this is clearly not the only factor operating. It means $(p\text{–}d)\pi$ conjugation must also play an effective role in this type of complex. The $(3p\text{–}3d)\pi$ conjugation in the chromium complex when sulphur inversion occurs will produce more effective overlap than the $(3p\text{–}5d)\pi$ overlap in the tungsten analogue and will lead to a lowering of the inversion barrier in the chromium complex to such an extent that the order of inversion energies, as expressed by $\Delta G^{\ddagger}$, becomes W > Cr > Mo. Similar rationalisations may account for the parallel trend in selenium-inversion energies where $(4p\text{–}nd)\pi$ conjugation (n = 3, 4, and 5 for Cr, Mo, and W respectively) will occur.

In Table 5 it will be observed that the energy for inversion in the selenium complexes is *ca.* 20 kJ mol^{-1} higher than that for corresponding sulphur analogues. This is fully in accord with previous results.[4,25–29]

Thus, the relative magnitudes of the electronegativity and conjugation effects control the order of $\Delta G^{\ddagger}$ values for the inversion process. With $\Delta G^{\ddagger}$ values for the complexes being in the order of W > Cr > Mo and Se > S, the conjugation effect dominates the electronegativity influence.

Some recent studies[6,19] on open-chain ligand complexes of type $[\mathrm{M(CO)_5(Me_3SiCH_2EECH_2SiMe_3)}]$ (M = Cr, Mo, or W) allow an assessment of the effect of introducing a pyramidal atom in a five-membered ring. Table 7 shows the effect to be very appreciable with $\Delta G^{\ddagger}$ values for S or Se inversion being increased by 10—14 kJ mol^{-1}. This is in accord with previous studies on inverting nitrogen[30] and chalcogen[31] atoms and is due to the ligand ring constraining access to the planar transition state of the inverting atom.

Table 5. Arrhenius and Eyring activation parameters for pyramidal inversion at co-ordinated sulphur or selenium in complexes of the type $[M(CO)_5(Me_2CCH_2EECH_2)]$

Complex						
M	E	E_a/kJ mol^{-1}	$\log_{10}(A/s^{-1})$	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	[a]$\Delta G^{\ddagger}$/kJ mol^{-1}
Cr	Se	68.07 ± 0.65	12.87 ± 0.11	65.58 ± 0.67	−6.9 ± 2.2	67.62 ± 0.10
Mo	Se	64.89 ± 1.49	13.56 ± 0.28	62.55 ± 1.48	6.8 ± 5.3	60.52 ± 0.18
W	Se	72.60 ± 1.66	13.38 ± 0.28	70.07 ± 1.67	2.3 ± 5.5	69.38 ± 0.13
Cr	S	64.28 ± 2.08	13.70 ± 0.46	62.33 ± 2.09	12.5 ± 8.9	47.58 ± 0.56
Mo	S	54.46 ± 0.78	13.93 ± 0.19	52.69 ± 0.78	15.9 ± 3.7	41.40 ± 0.31
W	S	54.68 ± 1.37	13.84 ± 0.31	52.76 ± 1.37	13.9 ± 6.0	48.61 ± 0.41

[a] Calculated for T = 298.15 K.

Table 6. Arrhenius and Eyring activation parameters for 1,2-metal shifts in Group 6 metal pentacarbonyl[a] complexes of 4,4-dimethyl-1,2-dithiacyclopentane and -diselenacyclopentane

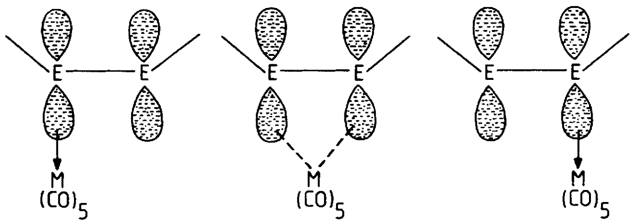
Complex	E_a/kJ mol^{-1}	$\log_{10}(A/s^{-1})$	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	[b]$\Delta G^{\ddagger}$/kJ mol^{-1}
$[Cr(CO)_5(Me_2CCH_2SSCH_2)]$	77.94 ± 2.07	12.72 ± 0.30	74.98 ± 2.08	−11.2 ± 5.9	78.31 ± 0.34
$[Mo(CO)_5(Me_2CCH_2SSCH_2)]$	75.73 ± 3.51	13.83 ± 0.58	73.09 ± 3.53	11.0 ± 11.1	69.80 ± 0.21
$[W(CO)_5(Me_2CCH_2SSCH_2)]$	77.55 ± 3.22	12.38 ± 0.46	74.50 ± 3.23	−17.9 ± 8.8	79.83 ± 0.61
$[Cr(CO)_5(Me_2CCH_2SeSeCH_2)]$	81.48 ± 0.31	12.87 ± 0.04	78.53 ± 0.29	−8.3 ± 0.8	81.02 ± 0.05
$[W(CO)_5(Me_2CCH_2SeSeCH_2)]$	86.48 ± 1.42	13.42 ± 0.20	83.44 ± 1.45	2.0 ± 4.0	82.83 ± 0.27

[a] Not determined for $[Mo(CO)_5(Me_2CCH_2SeSeCH_2)]$. [b] At 298.15 K.

Table 7. Comparison of $\Delta G^{\ddagger}$/kJ mol^{-1} data for $[M(CO)_5(Me_3SiCH_2EECH_2SiMe_3)]$ (1)* and $[M(CO)_5(Me_2CCH_2EECH_2)]$ (2)

M	E	(1)	(2)	(2)−(1)
Inversion energies				
Cr	Se	53.0	67.6	14.6
Mo	Se	49.7	60.5	10.8
W	Se	54.8	69.4	14.6
W	S	37.3	48.6	11.3
1,2-Metal shifts				
Cr	S	70.4	78.3	7.9
Cr	Se	75.5	81.0	5.5
Mo	S	62.6	69.8	7.2
W	S	74.2	79.8	5.6
W	Se	78.4	82.8	4.4

* Refs. 6 and 19.



Scheme 3. Proposed mechanism for the 1,2-metal shift process

1,2-Metal Shift Process.—At higher temperatures, when pyramidal inversion is fast, commutation of the $M(CO)_5$ moiety occurs between adjacent chalcogen atoms *via* 1,2-metal jumps. It is assumed that this intramolecular 1,2 commutation passes through a seven-co-ordinated transition state in which the lone pairs on the adjacent E atoms are both co-ordinated, albeit rather weakly, to the $M(CO)_5$ moiety (Scheme 3).

A comparison of $\Delta G^{\ddagger}$ values for $M(CO)_5$ commutation shows the same trend, namely W > Cr > Mo and Se > S, as for pyramidal inversion. The corresponding $\Delta G^{\ddagger}$ values for 1,2-metal shifts of the co-ordinated selenium ligands are *ca.* 3 kJ mol^{-1} higher than those for the sulphur complexes. For metal variation, the 1,2-jump barrier in tungsten complexes is 2 kJ mol^{-1} higher than that for chromium which is already 8 kJ mol^{-1} greater in comparison with molybdenum. The order of 1,2-shift barriers, *i.e.* W > Cr > Mo, is independent of whether co-ordination occurs through sulphur or selenium. The higher value for tungsten complexes is once again expected to arise from the combined influences of $(p\text{–}d)\pi$ conjugation and electronegativity. The slightly lower energy barriers for sulphur complexes compared to selenium complexes may be due to the slightly shorter commuting distances involved. The same trend has been observed for 1,2 shifts in the open-chain complexes $[M(CO)_5(Me_3SiCH_2EECH_2SiMe_3)]$ (M = Cr, Mo, or W)[19] and for 1,3 shifts in $[M(CO)_5(MeECH_2E'Me)]$ (M = Cr, Mo, or W; E = E′ = S or Se, E = S, E′ = Se).[7,32]

The effect of ring incorporation of the E atoms on their 1,2-shift energies is apparent in Table 7. An increase in $\Delta G^{\ddagger}$ of 4—8 kJ mol^{-1} consistently accompanies ring incorporation and mirrors the effect on the inversion energies but to a lesser extent. This supports the underlying suggestion in these studies that metal fluxional shifts only become accessible when pyramidal inversions are rapid in the n.m.r. sense.

The absence of any observable 1,2 shifts in the naphthalene-type ligand complexes $[M(CO)_5(C_{10}H_6EE')]$ is somewhat surprising at first sight. However, it is probably a consequence of the lower *solution* stabilities of these complexes compared to the other five-membered ring complexes which precluded high-temperature n.m.r. measurements (ambient to *ca.* 85 °C) without accompanying decomposition. There would seem to be no obvious structural reasons why 1,2-metal shifts should not occur in these complexes.

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