Pyramidal Inversions and 1,2-Metal Shifts in Pentacarbonyl-chromium, -molybdenum, and -tungsten Derivatives of Dialkyl Disulphides and Dialkyl Diselenides. A Nuclear Magnetic Resonance Investigation†

Edward W. Abel, Suresh K. Bhargava, Pramod K. Mittal, Keith G. Orrell, and Vladimir Šik
Department of Chemistry, The University, Exeter EX4 4QD

Variable-temperature ^1H n.m.r. spectra of the mononuclear complexes $[M(CO)_5(Me_3SiCH_2EECH_2SiMe_3)]$ (M = Cr, Mo, or W; E = S or Se) have established the occurrence of two distinct internal dynamic phenomena. The co-ordinated S or Se atom undergoes facile pyramidal inversion whilst at above-ambient temperatures a novel 1,2-metal shift between the adjacent pair of chalcogen atoms of the ligands occurs. Energy data for both processes have been computed by total n.m.r. band-shape analyses.

Sulphur and selenium complexes of transition metals have been shown to exhibit a strikingly wide range of fluxional phenomena.[1,2] In mononuclear complexes pyramidal inversions of the co-ordinated chalcogen atoms commonly induce considerable reorganisation of the metal–chalcogen bonding, leading in many cases to metallotropic shifts. In the case of complexes of Cr, Mo, or W, 1,3-metallotropic shifts have been reported for the cyclic ligand complexes $[M(CO)_5(SCHRSCHRSCHR)]$ (R = H or Me)[3] and $[M(CO)_5(SCH_2SCH_2SCH_2SCH_2)]$.[4] In fact, 1,3 metal–chalcogen bond movements are not uncommon, having been observed, as ligand-switching or pivoting movements, in dinuclear complexes of $[(PtXMe_3)_4]$ with $MeSCH_2SMe$,[5] $MeSeCH_2SeMe$,[5] $MeSCH_2SeMe$,[6] and $SCHRSCHRECHR$ (E = S or CH_2).[7] In view, therefore, of the wide occurrence of 1,3 metal–chalcogen shifts we sought to ascertain whether simple 1,2 metal–chalcogen shifts might occur. Literature precedents for 1,2 shifts are quite sparse and all involve nitrogen atoms. Thus, 1,2-fluxional shifts have been reported in open-chain ligand complexes of 1,2-dimethyldiazene,[8] 1,2-di-isopropyldiazene,[9] *cis*-azobenzene,[10] and in cyclic ligand complexes of benzo[*c*]cinnoline.[11] However, in view of our experience with complexes of sulphur and selenium ligands we chose to prepare and investigate the mononuclear complexes $[M(CO)_5(Me_3SiCH_2EECH_2SiMe_3)]$ (M = Cr, Mo, or W; E = S or Se). We now report definitive and quantitative evidence for the occurrence of 1,2-metal shifts in these complexes, in addition to the expected pyramidal inversions of the S or Se atoms. A portion of this work has already been communicated.[12]

Experimental

Materials.—Tetraethylammonium bromopentacarbonylmetalates, $[NEt_4][M(CO)_5Br]$ (M = Cr, Mo, *or* W). Dried tetraethylammonium bromide (3.78 g, 18 mmol) was heated with an excess of metal hexacarbonyl (23 mmol, purified by sublimation) in $O(CH_2CH_2OMe)_2$ (200 cm^3) at an expedient temperature (Cr, *ca.* 135 °C; Mo, *ca.* 80—85 °C; W, *ca.* 120 °C), under dry nitrogen. Completion of the reaction was marked by the cessation of evolution of carbon monoxide. Filtration while hot under nitrogen, followed by addition of an equal amount of light petroleum (b.p. 40—60 °C) and cooling to -5 °C for *ca.* 6 h, gave yellow crystals of tetraethylammonium bromopentacarbonylmetalate. The solvent was decanted, the crystals washed with light petroleum (b.p. 40—60 °C) and dried under vacuum. Any unreacted hexacarbonyl was removed by heating the crystals at 60 °C (0.001 mmHg) for *ca.* 2 h. Yield 90—95%.[13]

Triethyloxonium tetrafluoroborate $(Et_3O^+BF_4^-)$. This was prepared by the previously reported method[14] and stored over dry diethyl ether at -5 °C.

Organosilicon sulphur ligands. The following ligands were prepared by previously reported methods: trimethylsilylmethanethiol, b.p. 112—115 °C, η_D^{24} (589.3 nm) = 1.4515 [lit.,[15] 55 °C (93 mmHg), η_D^{24} = 1.4502]; bis(trimethylsilylmethyl) sulphide, b.p. 85 °C (12 mmHg) [lit.,[16] 71—73 °C (5 mmHg)]; bis(trimethylsilylmethyl) disulphide, b.p. 118—120 °C (10 mmHg), η_D^{24} = 1.4910 [lit.,[17] 82 °C (1 mmHg), η_D^{25} = 1.4906].

Organosilicon selenium ligands. Bis(trimethylsilylmethyl) selenide and diselenide. Trimethylsilylmethylmagnesium bromide, prepared from trimethylsilylmethyl bromide (58.8 g, 0.35 mol) and magnesium (8.6 g, 0.36 mol) in dry ether (150 cm^3), was treated with dry selenium powder (29.0 g, 0.367 mol) at 0 °C. The reaction mixture was heated to reflux for 1 h. Subsequent hydrolysis with 40% hydrochloric acid at 0 °C gave two layers; the upper orange-red layer was separated and fractionally distilled under reduced pressure. Two major fractions were collected: first a pale yellow liquid [b.p. 92 °C (15 mmHg)] which was characterised as *bis(trimethylsilylmethyl) selenide* (11.0 g, 49.6%), and second an orange-red liquid [b.p. 134 °C (15 mmHg)] characterised as *bis(trimethylsilylmethyl) diselenide* (12.0 g, 41.3%).

Complexes $[M(CO)_5(Me_3SiCH_2EECH_2SiMe_3)]$ (M = Cr, Mo, *or* W; E = S *or* Se).—All the complexes were prepared in a similar manner and a single representative example is described.

To a stirred solution of tetraethylammonium bromopentacarbonyltungstate (0.896 g, 1.49 mmol) in dichloromethane (40 cm^3, freshly distilled from CaH_2) was added an excess of bis(trimethylsilylmethyl) diselenide (0.731 g, 2.2 mmol). This was followed by dropwise addition of a pre-cooled solution of triethyloxonium tetrafluoroborate (0.31 g, 1.49 mmol) in dichloromethane (10 cm^3). The colour of the solution changed from yellow to orange-red. All volatile materials were removed under reduced pressure and the residue was extracted with freshly distilled hexane. The extract was filtered (Schlenk) and concentrated under vacuum. Crystallisation from this solution at -20 °C yielded orange-red needles of *[bis(trimethylsilylmethyl) diselenide-*Se*]pentacarbonyltungsten*(o) (0.5 g, 46%).

An alternative method of preparation for these complexes is the action of the ligand on the appropriate pentacarbonyl(tetrahydrofuran)metal precursor.[18]

All solutions of these complexes were extremely air sensitive

---

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

Table 1. Characterisation of the complexes $[M(CO)_5(Me_3SiCH_2EECH_2SiMe_3)]$ and $[W(CO)_5(Me_3SiCH_2ECH_2SiMe_3)]$

			Elemental analysis (%)[b]				I.r. data: $\tilde{\nu}(CO)^c/cm^{-1}$	
Complex[a]	Colour	M.p./°C	C	H	S,Se	M	In hexane	In Nujol mull
(1) $[Cr(CO)_5(Me_3SiCH_2SSCH_2SiMe_3)]$	Yellow	45—46	36.45 (36.25)	5.15 (5.15)	15.00 (14.9)	13.05 (12.1)	2 067w, 1 989w, 1 948 (sh), 1 944s, 1 931m	2 073w, 1 989w, 1 951 (sh), 1 944s, 1 932m
(2) $[Cr(CO)_5(Me_3SiCH_2SeSeCH_2SiMe_3)]$	Orange	55 (decomp.)	29.75 (29.75)	4.25 (4.20)	29.85 (30.1)	9.85 (9.90)	2 060w, 1 987w, 1 953 (sh), 1 947s, 1 938m	2 072w, 1 989vw, 1 949 (sh), 1 946s, 1 935m
(3) $[Mo(CO)_5(Me_3SiCH_2SSCH_2SiMe_3)]$	Yellow	46—47 (decomp.)	32.75 (32.9)	4.70 (4.65)	 (13.5)	19.9 (20.2)	2 081w, 1 992w, 1 959s, 1 955 (sh), 1 938m	2 080w, 1 990w, 1 955s, 1 950 (sh), 1 934m
(4) $[Mo(CO)_5(Me_3SiCH_2SeSeCH_2SiMe_3)]$	Dark red-brown	54—55 (decomp.)	27.4 (27.45)	4.00 (3.90)	27.4 (27.8)	15.1 (16.9)	2 075w, 1 989w, 1 953s, 1 935m	2 077w, 1 988w, 1 951s, 1 936m
(5) $[W(CO)_5(Me_3SiCH_2SSCH_2SiMe_3)]$	Pale yellow	55—57 (decomp.)	27.6 (27.75)	3.95 (3.95)	 (11.4)	32.25 (32.7)	2 069w, 1 988w, 1 947s, 1 934m	2 082w, 1 990w, 1 947 (sh), 1 944s, 1 933m
(6) $[W(CO)_5(Me_3SiCH_2SeSeCH_2SiMe_3)]$	Orange- red	66—67 (decomp.)	23.8 (23.8)	3.35 (3.35)	24.05 (24.05)	28.0 (28.0)	2 075w, 1 990w, 1 952s, 1 940m	2 084w, 1 988vw, 1 947s, 1 933m
(7) $[W(CO)_5(Me_3SiCH_2SCH_2SiMe_3)]$	Yellow	63—64	28.75 (29.45)	3.85 (4.20)			2 075w, 1 987w, 1 942s, 1 932 (sh)	2 080w, 1 982w, 1 937s, 1 926 (sh)
(8) $[W(CO)_5(Me_3SiCH_2SeCH_2SiMe_3)]$	Pale yellow	67—68	27.05 (27.05)	3.60 (3.85)			2 066w, 1 983w, 1 936s, 1 934 (sh)	2 080w, 1 935s, 1 923 (sh)

[a] All the compounds were isolated as needle-shaped crystals which were fairly stable in air. All solutions in common organic solvents were, however, unstable on exposure to air, the relative stabilities being in the order W > Cr > Mo, with selenium complexes more stable than their sulphur counterparts. [b] Calculated values are given in parentheses. [c] Complexes of type $[M(CO)_5L]$ where L is regarded as a point ligand should exhibit the three ($2A_1$ and E) CO i.r.-active stretching vibrations of the C_{4v} point group. However, where the ligand is a bulky group, the symmetry is reduced and four or five stretching modes are observed (E. W. Ainscough, A. M. Brodie, and A. R. Furness, *Chem. Commun.*, 1971, 1357). In this table one band (*ca.* 1 986—1 990 cm^{-1}) is attributed to the small amount of $[M(CO)_6]$ present due to decomposition (H. Schumann, *Chem. Ber.*, 1971, **104**, 993; W. Erhl and H. Vahrenkamp, *ibid.*, 1970, **103**, 3563), but the other extra band present in some spectra is presumed due to the effect of the bulky ligand. m = medium, sh = shoulder, s = strong, v = very, and w = weak.

and all reactions and manipulations were performed below room temperature (at *ca.* 0 °C) under an atmosphere of dry nitrogen using freshly distilled anhydrous solvents. Elemental analysis and i.r. spectral data for all the complexes are given in Table 1.

Spectra.—Infrared. I.r. spectra of the complexes in the metal carbonyl region were recorded either for hexane solutions or Nujol mulls on Perkin-Elmer 299B or 398 spectrophotometers.

N.m.r. N.m.r. samples were contained in a standard 5-mm tube fitted with a Taperlok joint (Wilmad Glass Co. Inc.) to avoid rapid decomposition of the solutions in air. The appropriate solvent (usually CD_2Cl_2 or C_6D_6) and reference material were distilled under vacuum onto the solid in the tube which was then filled with an atmosphere of dry nitrogen. Even with these precautions fresh samples had to be prepared at regular intervals during the above-ambient n.m.r. measurements.

Variable-temperature ^1H n.m.r. spectra were recorded using a JEOL PS/PFT-100 spectrometer operating at 100 MHz. Sample temperatures were controlled by a standard JES-VT-3 accessory and measured with a digital thermometer (Comark Ltd.). Temperatures are accurate to at least ±1 °C over the range studied. N.m.r. band-shape analyses were carried out as described previously.[5]

Results

Low-temperature N.M.R. Studies.—The four complexes $[M(CO)_5(Me_3SiCH_2EECH_2SiMe_3)]$ (M = Cr, Mo, or W, E = Se; M = W, E = S) gave similar spectra, one notable difference being that line-shape changes occurred in the range −50 to −10 °C for the selenide complexes and in the range −110 to −75 °C for one of the sulphide analogues. The other sulphide complexes $[M(CO)_5(Me_3SiCH_2SSCH_2SiMe_3)]$ (M = Cr or Mo) exhibited no temperature dependence of their spectra in the observable low-temperature range, room temperature down to −110 °C.

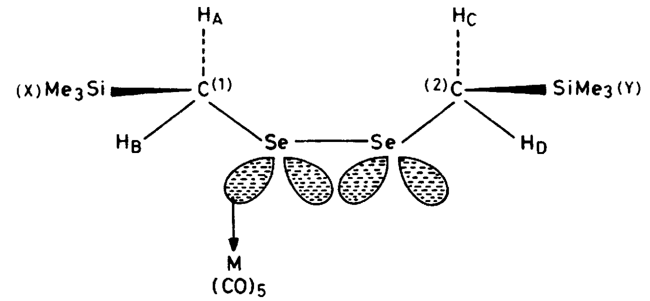

Figure 1. Static structure of $[M(CO)_5(Me_3SiCH_2SeSeCH_2SiMe_3)]$ complexes. Labelling is in accordance with text and Tables 2 and 4

The ^1H n.m.r. spectral variation with temperature is exemplified by the behaviour of the complex $[W(CO)_5(Me_3SiCH_2SeSeCH_2SiMe_3])$ whose structure is shown in Figure 1. In the static structure each methylene group contains diastereotopic hydrogen atoms (atoms A—D in Figure 1), and two AB quartets are observed (Figure 2) in the ^1H n.m.r. spectrum at −50 °C as expected for this structure. The AB quartet centred at higher frequency has a larger internal chemical shift and is therefore attributed to the methylene group attached to the co-ordinated selenium. On warming the sample the spectra clearly indicate the onset of a process which causes mutual exchange of the methylene-hydrogen environments, eventually leading to coalescence to a sharp averaged singlet at *ca.* 20 °C. These

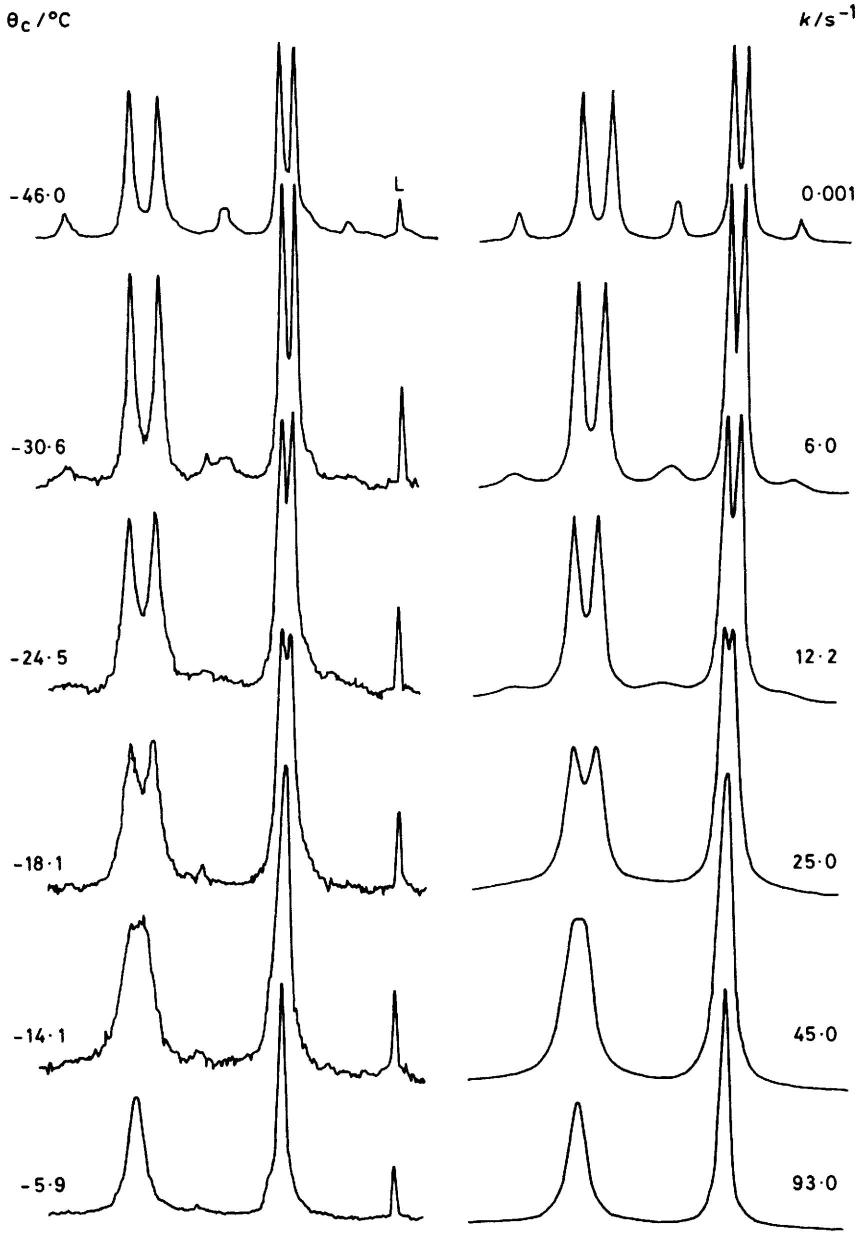

Figure 2. Experimental and computer-synthesised spectra of the methylene signals of [$W(CO)_5(Me_3SiCH_2SeSeCH_2SiMe_3)$] showing the effects of pyramidal selenium inversion; L indicates added free ligand

changes are clearly the result of pyramidal inversion of the metal-bonded selenium atom. Varying rates of rotation about W–Se, Se–Se, and/or Se–C bonds would not bring about such an averaging. In any case such bond rotations are likely to be fast on the n.m.r. time-scale as was exemplified by studies on the ligand bis(trimethylsilylmethyl) disulphide. Attempts to measure the S–S torsional barrier by n.m.r. spectroscopy failed because the S–S rotation was still too rapid at −125 °C, the lowest measurable temperature. Rotation about Se–Se bonds in both the free ligands and their metal complexes is likely to be even more facile.[19]

The nature of the inversion process in this complex is represented by the horizontal interconversions in Figure 3. The experimental spectra were simulated by computer analysis using the static parameters given in Table 2. The resulting 'optimum-fit' spectra are shown alongside the experimental spectra in Figure 2. These spectral changes are particularly notable in that the effects of pyramidal inversion are simultaneously transmitted to the proton environments both two and three bonds removed from the site of inversion. For this reason the fittings to the experimental spectra were very sensitive to the chosen rate constants, and the resulting energy data given in Table 3 are considered to be particularly reliable.

High-temperature N.M.R. Studies.—At temperatures well above those at which chalcogen pyramidal inversion was fast on the n.m.r. time-scale all six complexes [$M(CO)_5(Me_3SiCH_2EECH_2SiMe_3)$] (M = Cr, Mo, or W; E = S or Se) underwent a configurational change which was detectable in the range −18 to 85 °C. This configurational change when rapid on the n.m.r. time-scale caused the complexes to have an effective symmetry plane passing through, and at right angles to, the E–E bond in the complex. This resulted in the previously anisochronous trimethylsilylmethyl groups becoming equivalent at

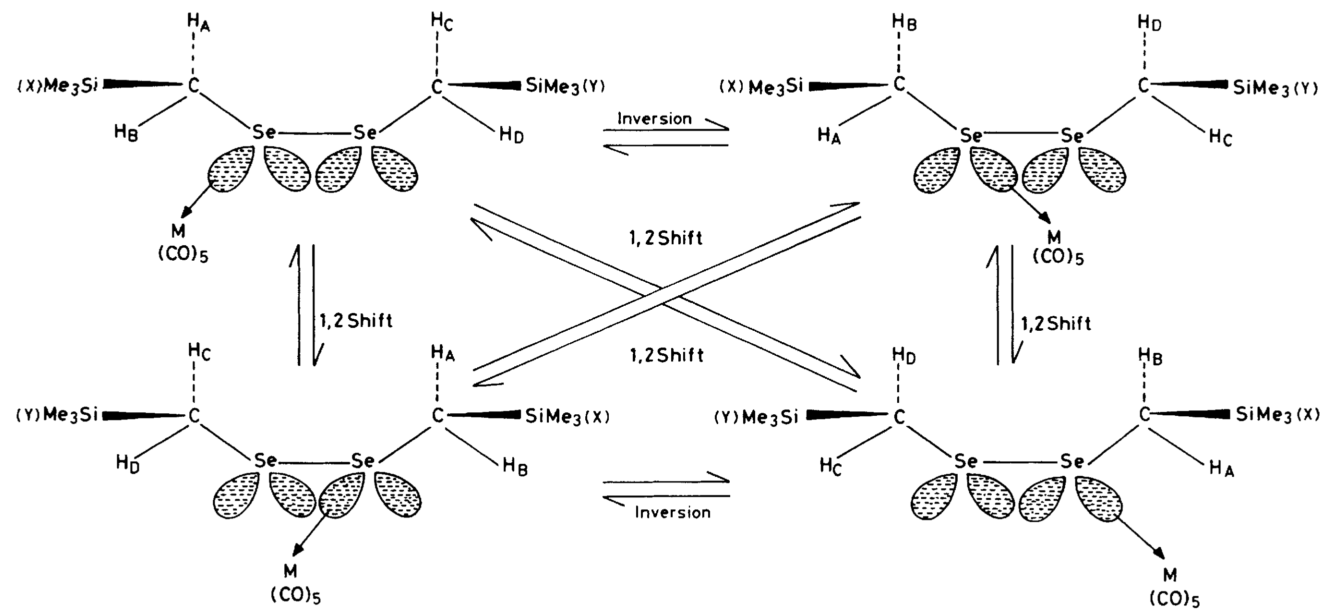

Figure 3. The effects of selenium inversion and 1,2-metal shifts on the methylene and methyl environments in $[M(CO)_5(Me_3SiCH_2SeSeCH_2SiMe_3)]$

Table 2. Static parameters used in the calculation of pyramidal inversion energies in complexes of the type $[M(CO)_5(Me_3SiCH_2EECH_2SiMe_3)]$. See Figure 1 for assignments

Complex			$C^{(1)}H_2$				$C^{(2)}H_2$			
M	E	θ_c/°C	ν_A[a]	ν_B	J_{AB}[b]	T_2^*/s	ν_C	ν_D	J_{CD}	T_2^*/s
Cr	Se	−69.5	278.0	257.5	13.2	0.180	266.7	259.6	11.0	0.180
Mo	Se	−69.0	277.8	256.5	13.1	0.121	259.1	253.2	11.1	0.140
W	Se	−46.0	299.3	285.3	12.9	0.186	267.2	258.7	11.0	0.220
W	S	−114.9	284.5	268.0	13.4	0.055	*c*	*c*	*c*	*c*
$[W(CO)_5(Me_3SiCH_2SeCH_2SiMe_3)]$		−39.6	240.0	223.4	13.7	0.185	240.0	223.4	13.7	0.185

[a] Chemical shifts (ν_i/Hz) measured relative to $SiMe_4$; solvent was either CD_2Cl_2 or CD_2Cl_2–CS_2. [b] ^2J/Hz. [c] Not calculated.

Table 3. Arrhenius and thermodynamic activation parameters for inversion at co-ordinated sulphur or selenium in the complexes $[M(CO)_5(Me_3SiCH_2EECH_2SiMe_3)]$

Complex				$\Delta G^‡$/kJ mol^{-1}		
M	E	E_a/kJ mol^{-1}	$\log_{10}A$	(at 298.15 K)	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
Cr	Se	53.6 ± 0.1	12.9 ± 0.1	53.0 ± 0.1	51.6 ± 0.1	−4.8 ± 0.5
Mo	Se	53.4 ± 0.4	13.4 ± 0.1	49.7 ± 0.1	51.4 ± 0.4	5.7 ± 1.8
W	Se	59.8 ± 0.8	13.7 ± 0.2	54.8 ± 0.1	57.7 ± 0.8	9.7 ± 3.0
W	S	38.2 ± 1.0	12.9 ± 0.3	37.3 ± 0.6	36.7 ± 1.0	−1.7 ± 5.6
$[W(CO)_5(Me_3SiCH_2SeCH_2SiMe_3)]$		62.2 ± 0.5	13.4 ± 0.1	58.5 ± 0.1	59.9 ± 0.5	4.6 ± 1.7

high temperatures. Thus, the two methylene singlets and the two methyl singlets coalesced and became individual singlets at high temperatures. These spectral changes were fitted in the usual way using standard procedures. Following the labelling previously used for the methylene protons, the spin problem for these protons was now of the type $\langle AB\rangle \rightleftharpoons \langle CD\rangle$. No account was taken of ^{77}Se–^1H couplings as these were barely visible in this region of the spectra. The spectral parameters on which the computer fittings were based are given in Table 4.

While the computations of these line-shape changes posed no difficulties, the recording of a reliable set of above-ambient temperature spectra certainly did. Despite the previously described precautions (see Experimental section), fresh samples had to be prepared for dynamic n.m.r. analysis every two or three temperatures, due to the rapid decomposition of the complex in solution. However, it proved possible to obtain satisfactory sets of spectra, which were perfectly reversible with temperature and were concentration independent, for all the complexes studied.

These spectral changes clearly imply an intramolecular commutation of the $M(CO)_5$ moiety over both chalcogen atom co-ordination sites *via* a 1,2-metal shift process (Figure 3). The intramolecular nature of the process was established by the complete absence of exchange upon addition of a small amount of free ligand. The Arrhenius and Eyring activation parameters calculated from the fittings to the methyl and, in some cases, the methylene signals are listed in Table 5.

Table 4. Static parameters for calculating energy barriers for 1,2-shift commutation in complexes of the type $[M(CO)_5(Me_3SiCH_2EECH_2SiMe_3)]$. See Figure 1 for assignments

Complex			$-CH_2-$			Me_3Si-		
M	E	θ_c/°C	$\nu_{(1)}$ [a]	$\nu_{(2)}$	T_2^*/s	ν_X	ν_Y	T_2^*/s
Cr	S	9.9	223.4	214.7	0.164	−0.8	−6.6	0.180
Cr	Se	33.0	248.9	235.2	0.160	−3.3	−7.8	0.286
Mo	S*	−18.0	252.7	236.3	0.202	20.4	15.0	0.241
Mo	Se*	−5.7	272.6	259.3	0.191	18.8	14.2	0.305
W	S	25.0	247.0	221.0	0.230	−6.2	−6.2	0.352
W	Se	40.2	270.1	233.8	0.164	−3.4	−7.6	0.380

[a] Chemical shifts (ν_i/Hz) measured relative to $SiMe_4$; solvent was C_6D_6, except when $CDCl_3$ was used (*).

Table 5. Energy parameters for 1,2-shift commutation in the complexes of the type $[M(CO)_5(Me_3SiCH_2EECH_2SiMe_3)]$

Complex						
M	E	E_a/kJ mol^{-1}	$\log_{10}A$	$\Delta G^‡$/kJ mol^{-1} (at 298.15 K)	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
Cr	S	72.4 ± 1.5	13.1 ± 0.2	70.4 ± 0.1	69.8 ± 1.5	−2.0 ± 4.7
Cr	Se	75.8 ± 0.8	12.8 ± 0.1	75.5 ± 0.1	73.1 ± 0.8	−8.2 ± 2.4
Mo	S	67.3 ± 0.6	13.6 ± 0.1	62.6 ± 0.1	64.9 ± 0.6	7.7 ± 2.2
Mo	Se	69.3 ± 2.1	13.2 ± 0.4	67.1 ± 0.1	66.8 ± 2.1	−1.2 ± 7.1
W	S	74.4 ± 1.8	12.8 ± 0.3	74.2 ± 0.2	71.6 ± 1.8	−8.7 ± 5.4
W	Se	82.7 ± 1.6	13.5 ± 0.2	78.4 ± 0.2	79.8 ± 1.6	4.7 ± 4.7

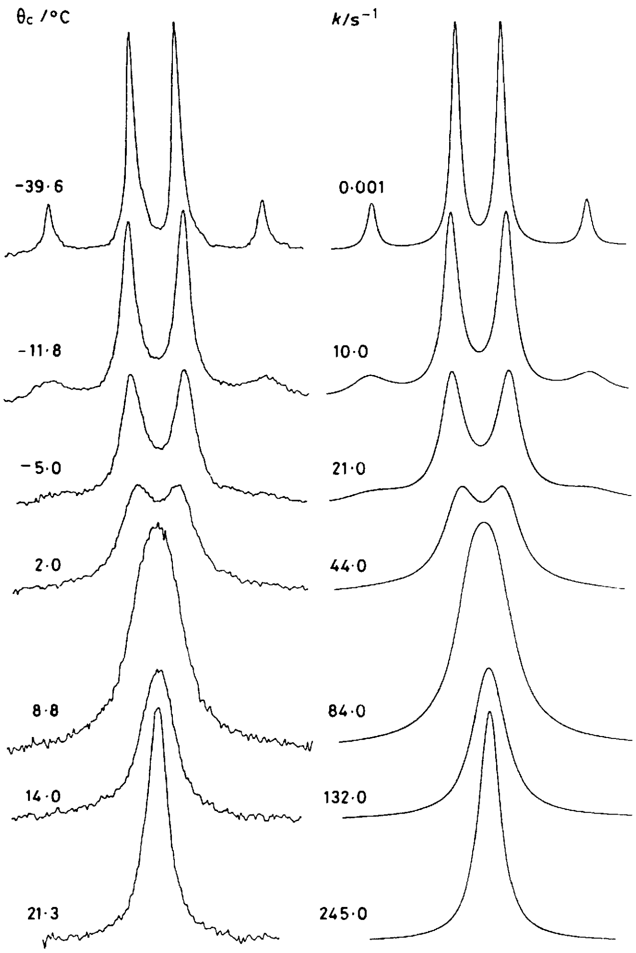

Figure 4. Experimental and computer-synthesised spectra of the methylene region of $[W(CO)_5(Me_3SiCH_2SeCH_2SiMe_3)]$ showing the effects of selenium inversion

Complexes of the Type $[W(CO)_5(Me_3SiCH_2ECH_2SiMe_3)]$ (E = S *or* Se).—The influence on chalcogen inversion of the contiguous non-inverting chalcogen was examined by preparing the above monochalcogenide complexes. Analytical and i.r. data for both complexes are included in Table 1 and both complexes were subsequently subjected to dynamic n.m.r. spectroscopy. In the case of the sulphur ligand complex, the diastereotopic methylene protons were virtually isochronous even at a temperature of −110 °C when a single broadened absorption was detected. At higher temperatures a sharp singlet was observed indicative of rapid sulphur inversion. No inversion-energy data could therefore be computed in this case. The selenium complex, however, exhibited well resolved spectra even at −40 °C (Figure 4) and the collapse of the AB quartet with increasing temperature was computed in the usual way. The energy data for this monochalcogenide complex are included in Table 3 for comparison with the dichalcogenide data.

Discussion

Chalcogen Pyramidal Inversion.—A recent review[2] has identified five factors which influence atomic inversion barriers, namely the nature of the inverting centre, the nature of the metal centre, π-conjugation effects in the ligands, ring strain in cyclic ligands, and *trans*-influence effects. The present studies provide data in relation to the first three factors.

Nature of the inverting centre. In the case of Group 6B elements previous data in the literature point to the inversion barriers being in the order Te > Se > S. This is clearly the case in the present complexes where the barrier for selenium inversion is 17.5 kJ mol^{-1} greater than that for sulphur inversion in the corresponding complex. Sulphur-inversion barriers were, in fact, too low to be measured in the cases of the chromium and molybdenum complexes, as evidenced by the temperature independence of their low-temperature spectra. The sulphur-inversion barrier measured for the complex $[W(CO)_5(Me_3SiCH_2SSCH_2SiMe_3])$ represents one of the lowest values recorded by ^1H dynamic n.m.r. analysis.

Table 6. Chalcogen inversion in various complexes of Cr, Mo, and W

Compound	Electronegativity of metal[a]	$\Delta G^{\ddagger}$/kJ mol^{-1} for chalcogen inversion[b]	Ref.
$[Cr(CO)_5(Me_3SiCH_2SeSeCH_2SiMe_3)]$	1.56	53.0	Present work
$[Mo(CO)_5(Me_3SiCH_2SeSeCH_2SiMe_3)]$	1.30	49.7	
$[W(CO)_5(Me_3SiCH_2SeSeCH_2SiMe_3)]$	1.40	54.8	
$[Cr(CO)_4(PhCH_2SCH_2CH_2SCH_2Ph)]$	1.56	51.9	*c*
$[Mo(CO)_4(PhCH_2SCH_2CH_2SCH_2Ph)]$	1.30	45.8	
$[W(CO)_4(PhCH_2SCH_2CH_2SCH_2Ph)]$	1.40	52.9	
$[Cr(CO)_4(MeSeCH_2CMe_2CH_2SeMe)]$	1.56	61.6	*d*
$[Mo(CO)_4(MeSeCH_2CMe_2CH_2SeMe)]$	1.30	56.6	
$[W(CO)_4(MeSeCH_2CMe_2CH_2SeMe)]$	1.40	62.9	
$[Cr(CO)_4(Me_2DCSeCD_2CH_2SeCDMe_2)]$	1.56	63.4	*e*
$[Mo(CO)_4(Me_2DCSeCD_2CH_2SeCDMe_2)]$	1.30	59.8	
$[W(CO)_4(Me_2DCSeCD_2CH_2SeCDMe_2)]$	1.40	65.9	

[a] Allred-Rochow values (A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, 1958, **5**, 264). [b] Mean values in some cases. [c] R. J. Cross, G. Hunter, and R. C. Massey, *J. Chem. Soc., Dalton Trans.*, 1976, 2015. [d] G. Hunter and R. C. Massey, *J. Chem. Soc., Dalton Trans.*, 1975, 209. [e] G. Hunter and R. C. Massey, *J. Chem. Soc., Dalton Trans.*, 1976, 2007.

Nature of the metal centre. Co-ordination of a sulphur or selenium atom to a transition metal is now well known to reduce drastically the chalcogen-inversion energy and bring it very suitably within the range of n.m.r. detection. This is certainly the case for the three selenium complexes studied. In the case of the sulphur complexes, the chromium and molybdenum atoms have accelerated the sulphur-inversion processes to such an extent that they are too rapid with respect to the n.m.r. detection time-scale (*i.e.* barriers are $<$ *ca.* 30 kJ mol^{-1}). This is in stark contrast to the case of sulphoxides[20] where barriers may be as high as 180 kJ mol^{-1}. The presence of the metal can have two major effects. First, it will decrease the *s* character of the lone-pair ground state in accordance with the electropositive nature of the metal. This will then allow easier access to the transition state in which the inverting lone pair of electrons is regarded as having pure *p* character. Secondly, there is the effect of $(p\text{–}d)\pi$ conjugation between the chalcogen and the metal, which will also stabilise the planar transition state. Table 6 illustrates the dependence of chalcogen inversion on transition metal for the present complexes and some related complexes. The data reveal that inversion barriers in the molybdenum complexes are *ca.* 3.5—6 kJ mol^{-1} lower than in the chromium complexes which in turn are *ca.* 1—2.5 kJ mol^{-1} lower than in the tungsten complexes. If only electronegativity effects are considered the order of inversion barriers should be Cr > W > Mo. Thus, on electronegativity arguments alone the inversion energies of the chromium species should be a little higher in each case. However, $(3p\text{–}3d)\pi$ conjugation (for sulphur) or $(4p\text{–}3d)\pi$ conjugation (for selenium) in the chromium complexes is likely to be more effective than the $(3p,4p\text{–}4d)\pi$ or $(3p,4p\text{–}5d)\pi$ conjugation in the molybdenum and tungsten complexes. This might then account for the barriers in the chromium complexes falling below those of the tungsten complexes.

Effect of chalcogenic substitution. In Table 3 it can be seen that the selenium-inversion barrier in a diselenide complex is *ca.* 4 kJ mol^{-1} lower than in the corresponding monoselenide complex. Exactly analogous data for sulphur inversion could not be obtained since sulphur inversion in the complex $[W(CO)_5(Me_3SiCH_2SCH_2SiMe_3)]$ could not be arrested sufficiently due to the small internal chemical shift of the diastereotopic methylene protons. However, data were available[21] for the closely analogous open-chain ligand complex $[W(CO)_5(MeSCH_2SCH_2SMe)]$. For this complex, the $\Delta G^{\ddagger}$ value for sulphur inversion was 42.5 kJ mol^{-1}, which should be compared with the value of 37.3 kJ mol^{-1} for the complex $[W(CO)_5(Me_3SiCH_2SSCH_2SiMe_3)]$ (Table 3). The presence of a contiguous chalcogen atom therefore clearly decreases the barrier to chalcogen inversion and may be explained in terms of π-conjugation effects, $(3p\text{–}3p)$ or $(4p\text{–}4p)$ for sulphur or selenium atoms respectively. Similar trends have been noted in the cases of diphosphines and diarsines.[22–24]

1,2-*Metal Shifts.*—The energy parameters for this novel commutation of the $M(CO)_5$ moiety were obtained for all six complexes (Table 5). Certain trends are immediately apparent. The energies of the 1,2 metal–sulphur shifts are 4—5 kJ mol^{-1} lower than for 1,2 metal–selenium fluxions in analogous complexes. This mirrors the trend in sulphur- and selenium-inversion energies. It thus poses the question as to whether rapid pyramidal inversion is an essential preliminary to 1,2- or, indeed, 1,3-metal shifts.[25] Certainly our observations to date point in that direction. The higher barriers in the diselenide complexes could be related to the somewhat greater distances between the two selenium co-ordination sites compared to the two sulphur sites, but electronic factors are also likely to play a part. This is the first observation of 1,2-metal shifts in dichalcogen metal complexes and so no comparison with other relevant energy data are possible at present. It should be noted, however, that 1,3-metal shifts in the complexes $[W(CO)_5L]$ (L = $MeSCH_2SMe$ or $MeSeCH_2SeMe$) follow the same trend.[25]

The $\Delta G^{\ddagger}$ values for the 1,2-shift process lie in the range 60—80 kJ mol^{-1} but the variation with transition metal is appreciable and significant. The trend is W > Cr > Mo with the energies for the tungsten complexes being *ca.* 4 kJ mol^{-1} higher than for the chromium complexes and the latter *ca.* 8 kJ mol^{-1} higher than those for the molybdenum complexes. The trend is independent of whether co-ordination occurs *via* sulphur or selenium, and is again analogous to that of pyramidal inversion. The n.m.r. observations do not give any insight into the mechanism of the 1,2-metal fluxion, but it is most likely to involve an intermediate in which the lone-pair orbitals on the adjacent chalcogen atoms are both co-ordinated, albeit rather weakly, to the $M(CO)_5$ moiety.

Acknowledgements

We are grateful for the generous support of the Commonwealth Scholarship Commission, U.K., and the University Grants Commission, India (to S. K. B.). We also thank the University of Exeter for a Scholarship (to P. K. M.).

References

1 E. W. Abel, *Chimia*, 1981, **35**, 100.
2 E. W. Abel, S. K. Bhargava, and K. G. Orrell, *Prog. Inorg. Chem.*, 1984, **32**, 1.
3 E. W. Abel, M. Booth, K. G. Orrell, and G. M. Pring, *J. Chem. Soc., Dalton Trans.*, 1981, 1944.
4 E. W. Abel, G. D. King, K. G. Orrell, and V. Šik, *Polyhedron*, 1983, **2**, 1363.
5 E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Šik, *J. Chem. Soc., Dalton Trans.*, 1980, 2208.
6 E. W. Abel, K. Kite, K. G. Orrell, V. Šik, and B. L. Williams, *J. Chem. Soc., Dalton Trans.*, 1981, 2439.
7 E. W. Abel, M. Booth, G. D. King, K. G. Orrell, G. M. Pring, and V. Šik, *J. Chem. Soc., Dalton Trans.*, 1981, 1846.
8 M. N. Ackermann, D. J. Dobmeyer, and L. C. Hardy, *J. Organomet. Chem.*, 1979, **182**, 561.
9 M. N. Ackermann, R. M. Willett, M. H. Englert, C. R. Barton, and D. B. Shewitz, *J. Organomet. Chem.*, 1979, **175**, 205.
10 C. C. Frazier III and H. Kisch, *Inorg. Chem.*, 1978, **17**, 2736.
11 M. Kooti and J. F. Nixon, *J. Organomet. Chem.*, 1976, **105**, 217.
12 E. W. Abel, S. K. Bhargava, P. K. Mittal, K. G. Orrell, and V. Šik, *J. Chem. Soc., Chem. Commun.*, 1982, 535.
13 E. W. Abel, I. S. Butler, and J. G. Read, *J. Chem. Soc.*, 1963, 2068.
14 H. Meerwein, *Org. Synth.*, 1966, **46**, 113.
15 G. D. Cooper, *J. Am. Chem. Soc.*, 1954, **76**, 2500.
16 A. O. Minklei, Q. W. Decker, and H. W. Post, *Recl. Trav. Chim. Pays-Bas.*, 1957, **76**, 187.
17 Q. W. Decker and H. W. Post, *J. Org. Chem.*, 1960, **25**, 249.
18 F. R. Hartley, S. G. Murray, W. Levason, H. E. Soutter, and C. A. McAuliffe, *Inorg. Chim. Acta*, 1979, **35**, 265.
19 E. W. Abel, M. Booth, C. A. Brown, K. G. Orrell, and R. L. Woodford, *J. Organomet. Chem.*, 1981, **214**, 93.
20 D. R. Rayner, A. J. Gordon, and K. Mislow, *J. Am. Chem. Soc.*, 1968, **90**, 4854.
21 E. W. Abel, M. Z. A. Chowdhury, K. G. Orrell, and V. Šik, *J. Organomet. Chem.*, 1984, **262**, 293.
22 R. D. Baechler and K. Mislow, *J. Am. Chem. Soc.*, 1971, **93**, 773.
23 J. B. Lambert, G. F. Jackson III, and D. C. Muller, *J. Am. Chem. Soc.*, 1970, **92**, 3093.
24 A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 400.
25 E. W. Abel, S. K. Bhargava, T. E. MacKenzie, P. K. Mittal, K. G. Orrell, and V. Šik, *J. Chem. Soc., Chem. Commun.*, 1982, 983.

Received 16*th July* 1984; *Paper* 4/1224