Heteronuclear 1,3-Intramolecular Metal Shifts in Pentacarbonyl-chromium, -molybdenum, and -tungsten Derivatives of 2-Thia-4-selenapentane. A Dynamic Nuclear Magnetic Resonance Investigation†

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The mononuclear complexes [$M(CO)_5(MeSeCH_2SMe)$] (M = Cr, Mo, or W) have been prepared and are present in solution as isomers with both S→M and Se→M bonding. In addition to the facile pyramidal atomic inversion of the metal-co-ordinated sulphur and selenium atoms, a novel 1,3-metal shift between the two different ligand atoms occurs. From static and dynamic n.m.r. studies the relative populations of sulphur- and selenium-bonded species have been obtained, along with the activation energy for both S→Se and Se→S metal shifts. Energy profiles for these 1,3-shifts reveal the distinction in ground-state energies between the sulphur- and selenium-bonded isomers and essentially quantify the difference in bond energy between the S→M and Se→M bonds; such values are not otherwise easily accessible.

In recent years the transition metal complexes of organosulphur and -selenium ligands have been observed to display a remarkable range of fluxional phenomena.[1] These have included 1,3-metallotropic shifts, which have been observed[2] and extensively investigated[3–5] for the cyclic-ligand complexes of pentacarbonyl-chromium, -molybdenum, and -tungsten. In the light, therefore, of the extensive occurrence of such 1,3-metal chalcogen shifts, we have sought to ascertain whether such shifts might occur in acyclic ligands. We report herein definitive evidence and quantitative characterization for the occurrence of 1,3-metal chalcogen shifts between the sulphur and selenium atoms in 2-thia-4-selenapentane. A preliminary report of this work has already appeared.[6]

Experimental

Materials.—Triethyloxonium tetrafluoroborate was prepared as previously reported[7] and stored in dry diethyl ether at −5 °C. Dichloromethane used in the preparation of metal complexes was refluxed and distilled from calcium hydride.

Tetraethylammonium bromopentacarbonylmetalates, [NEt_4][$M(CO)_5Br$] (M = Cr, Mo, *or* W).[8] Anhydrous tetraethylammonium bromide (*ca.* 13 mmol) was heated with an excess of metal hexacarbonyl (*ca.* 15.0 mmol) in dimethyldigol, $O(CH_2CH_2OMe)_2$, at an expedient temperature (Mo, 80—85; W, 120; Cr, 130—135 °C) under dry nitrogen until the steady evolution of carbon monoxide ceased. The solution was filtered hot under nitrogen, followed by addition of an equal volume of light petroleum (b.p. 40—60 °C), and cooling at −5 °C for *ca.* 8 h gave yellow crystals of the tetraethylammonium bromopentacarbonylmetalate. Solvent was decanted and the crystals washed with light petroleum (b.p. 40—60 °C; 3 × 50 cm^3) and dried at reduced pressure. Traces of unreacted hexacarbonyl were removed by treatment at 60 °C (0.001 mmHg) for *ca.* 2 h. The pure salts (yield 90—95%) were stored in darkness under nitrogen.

2-*Thia*-4-*selenapentane*.[9] A solution of sodium metal (5.06 g, 0.22 mmol) was prepared in liquid ammonia (500 cm^3) at −78 °C (acetone–CO_2 bath) over a period of 30 min. Dimethyl diselenide (17 g, 0.09 mol) was then added very slowly to the vigorously stirred deep blue solution. The mixture was stirred for 10 h allowing the ammonia to evaporate completely, and then 1-chloro-2-thiapropane (25.0 g, 0.26 mol) was added slowly to the residual solid. The mixture was then stoppered and shaken for 2 h after which the resulting suspension was stirred at 50 °C for 30 h. Water (200 cm^3) and chloroform (200 cm^3) were added to dissolve the sodium chloride and organic matter respectively. The layers were separated and the aqueous layer further extracted with chloroform (3 × 75 cm^3). After magnesium sulphate drying, chloroform was removed from the organic layer under reduced pressure and the residual liquid distilled to give the product as a pale yellow liquid (10.3 g, 64%), b.p. 65—66 °C (11 mmHg).

Preparation of the Metal Complexes [$M(CO)_5(MeSeCH_2SMe)$] (M = Cr, Mo, *or* W).—An excess of 2-thia-4-selenapentane (2.2 mmol) in dichloromethane (30 cm^3) was added to a stirred solution of tetraethylammonium bromopentacarbonylmetalate (1.8 mmol) in dichloromethane (30 cm^3) under nitrogen. After cooling the mixture to 0 °C, a pre-cooled solution of triethyloxonium tetrafluoroborate (1.8 mmol) in dichloromethane (10 cm^3) was added dropwise. The bright yellow colour of the solution was lost within 5 min.

All volatile materials were removed at reduced pressure and the solid residue extracted with freshly distilled hexane (3 × 30 cm^3). The combined extract was filtered through a Schlenk filter and the volume of the clear solution reduced (20 °C/20 mmHg) to *ca.* 15 cm^3. Cooling of this solution at −20 °C for *ca.* 20 h produced the crystalline product. Characterization of the three complexes is summarized in Table 1.

N.M.R. Spectra.—Solutions were prepared in standard 5-mm tubes fitted with Taperlock joints (Wilmad Glass Co. Inc.) to avoid decomposition due to air. The appropriate solvent and reference material were distilled under vacuum onto the solid sample in the tube which was then flushed with dry nitrogen. 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 recorded are accurate to at least ±1 °C over the ranges reported. N.m.r. bandshape analyses were carried out as previously described.[10]

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

Table 1. Characterization of the complexes [M(CO)$_5$L] (M = Cr, Mo, or W; L = MeSeCH$_2$SMe)

Complex[a]	Colour	M.p./°C	Analysis[b] (%) C	H	I.r.:[c] ν(CO)/cm^{-1}			
[Cr(CO)$_5$L]	Yellow	57—58	27.4 (27.7)	2.2 (2.3)	2 072m	1 982w	1 948 (sh)	1 939s
[Mo(CO)$_5$L]	Pale yellow	53—54	24.5 (24.6)	1.7 (2.1)	2 077m	1 988w	1 953 (sh)	1 940s
[W(CO)$_5$L]	Yellow	66	20.0 (20.1)	1.6 (1.7)	2 075m	1 981w	1 949 (sh)	1 938s

[a] Yields of pure recrystallized complex {based on [M(CO)$_6$]} were in the range 65—85%. All compounds formed needle-like crystals, which were stable in air for several hours. Solutions in common organic solvents were unstable to oxygen, and were made and kept under nitrogen. [b] Calculated values given in parentheses. [c] Hexane solution. The CO-stretching region of these [M(CO)$_5$L] compounds is more complex than the usual three ($2A_1 + E$) peaks expected for C_{4v} symmetry. This may be due to the presence of each compound in solution as two isomers with S→M and Se→M bonding; alternatively it could be a consequence of the bulky ligand L lowering the formal C_{4v} molecular symmetry of [M(CO)$_5$L].

Table 2. Percentage populations of the ligand linkage isomers in the complexes [M(CO)$_5$L] (M = Cr, Mo, or W)

Complex	Se Bonded	S Bonded
[Cr(CO)$_5$L]	80	20
[Mo(CO)$_5$L]	83	17
[W(CO)$_5$L]	76.5	23.5

Table 3. Static parameters and rate constants used in complete bandshape analysis of the methylene 400-MHz AB spectrum of [W(CO)$_5$(MeSeCH$_2$SMe)] (Se→W bonded)[a]

T/°C	ν_A/Hz	ν_B/Hz	$^2J_{AB}$/Hz	T_2*/s
−20.0	1 560.3	1 572.8	12.4	0.198

T/°C	−20.0	−5.0	0.0	5.0	10.0	20.0
k/s^{-1}	0.01	7.4	12.3	19.5	33.7	77.0

[a] Solvent CD$_2$Cl$_2$, internal reference SiMe$_4$; T_2* = relaxation time.

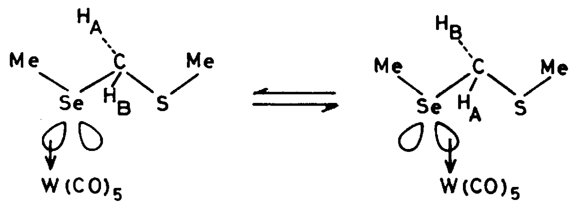

Figure 1. Pyramidal inversion about co-ordinated selenium in [W(CO)$_5$(MeSeCH$_2$SMe)], illustrating the equivalencing of the hydrogens in the prochiral methylene group

Results

Room-temperature ^{1}H *N.M.R. Studies.*—A striking feature of the spectra of the complexes [M(CO)$_5$(MeSeCH$_2$SMe)] (M = Cr, Mo, or W) was the presence in solution of two different ligand-linkage isomers due to ligand–metal attachment either *via* sulphur or selenium atoms. These isomers could not be isolated due to a slow intramolecular ligand site exchange (see below) but the relative percentage populations of the isomers were clearly discernible, and are noted in Table 2.

Low-temperature ^{1}H *N.M.R. Studies.*—Whilst at room temperature only the two sharp singlets for the methylene region are observed resulting from the isomers having Se→M and S→M bonding, at lower temperatures the methylene region is more complex. At −60 °C the 100-MHz spectrometer did not give well resolved spectra, but the 400-MHz ^{1}H spectra (University of Warwick) showed a clear AB quartet for each isomer. On warming, the low-intensity quartet of the sulphur-bonded isomer collapsed most rapidly, but at 20 °C both AB quartets were reduced to sharp singlets. Only the strong quartet of the selenium-bonded isomer was suitable for a quantitative study of the temperature-variable spectra and this was performed specifically with the complex [W(CO)$_5$(MeSeCH$_2$-SMe)]. The spectra were simulated by complete bandshape analysis on the basis of AB$\rightleftharpoons$BA spin interconversions. The static parameters used in the calculations are given in Table 3 along with the rate constants used in the computer-simulated best-fit spectra. Such a pyramidal inversion at co-ordinated selenium is illustrated in Figure 1.

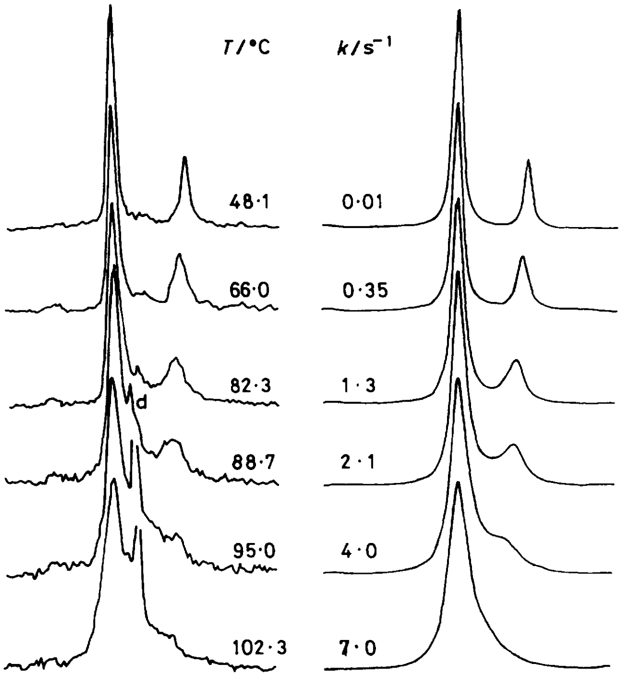

Figure 2. Variable-temperature 100-Mz ^{1}H n.m.r. spectra of the complex [W(CO)$_5$(MeSeCH$_2$SMe)] and their computer simulation, showing the effects of the 1,3-shifts (Se→S); d = decomposition product

High-temperature N.M.R. Studies.—Hydrogen-1 spectra at room temperature comprised, for each complex, two singlets for the methylene region and four signals for the methyl groups. Increase of temperature above ambient caused broadening and eventual coalescence of the two resonances of the methylene region to one singlet (Figure 2). Simultaneously the four methyl signals of each complex collapsed to two singlets at *ca.* 50, 90, and 100 °C for the Mo, Cr, and W complexes respectively. Further rise in temperature sharpened these peaks and all the changes were fully temperature reversible.

Table 4. Static ^1H n.m.r. parameters[a] used for calculating energy barriers for the 1,3-metal shifts in $[M(CO)_5(MeSeCH_2SMe)]$ complexes

		$-CH_2-$			$-CH_3$			
Complex	$T/°C$	ν_A	ν_B	T_2^*/s	ν_A	ν_B	T_2^*/s	Solvent
$MeSeCH_2SMe$, $MeSeCH_2SMe$ ↓ ↓ Cr Cr $(CO)_5$ $(CO)_5$	47.5	293.70	280.39	0.286	146.36	151.00[b]	0.343	C_6D_6
$MeSeCH_2SMe$, $MeSeCH_2SMe$ ↓ ↓ Mo Mo $(CO)_5$ $(CO)_5$	22.9	373.04	366.21	0.297	235.10	244.62[b]	0.387	$CDCl_3$
$MeSeCH_2SMe$, $MeSeCH_2SMe$ ↓ ↓ W W $(CO)_5$ $(CO)_5$	48.1	307.37	298.33	0.245	143.06	138.91[c]	0.286	$C_6D_5CD_3$

[a] Chemical shifts (ν_i/Hz) measured relative to hexamethyldisiloxane for M = Cr and W, and $SiMe_4$ for M = Mo. [b] Co-ordinated chalcogen atom methyls. [c] Unco-ordinated chalcogen atom methyls.

Table 5. Arrhenius and Eyring activation parameters for 1,3-metal shifts and Se inversion in $[M(CO)_5(MeSeCH_2SMe)]$ complexes

Complex	1,3-Metal shift	E_a/kJ mol^{-1}	$\log_{10}(A/s^{-1})$	$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ddagger$/ J K^{-1} mol^{-1}	$\Delta G^{\ddagger a}$/ kJ mol^{-1}
$MeSeCH_2SMe$, $MeSeCH_2SMe$ ↓ ↓ Cr Cr $(CO)_5$ $(CO)_5$	Se→S S→Se	85.59 ± 1.87 85.97 ± 1.80	12.98 ± 0.27 13.64 ± 0.26	82.57 ± 1.89 82.95 ± 1.80	−6.3 ± 5.2 6.3 ± 5.00	84.46 ± 0.34 81.08 ± 0.32
$MeSeCH_2SMe$, $MeSeCH_2SMe$ ↓ ↓ Mo Mo $(CO)_5$ $(CO)_5$	Se→S S→Se	78.75 ± 0.47 78.74 ± 0.47	13.49 ± 0.08 14.18 ± 0.08	76.00 ± 0.48 75.99 ± 0.48	4.1 ± 1.4 17.3 ± 1.5	74.77 ± 0.04 70.84 ± 0.04
$MeSeCH_2SMe$, $MeSeCH_2SMe$ ↓ ↓ W W $(CO)_5$ $(CO)_5$	Se→S S→Se	84.47 ± 3.18 87.44 ± 3.20	12.99 ± 0.46 13.50 ± 0.46	84.51 ± 3.16 84.48 ± 3.17	−6.00 ± 8.8 3.8 ± 8.8	86.29 ± 0.54 83.36 ± 0.54
$MeSeCH_2SMe$[b] ↓ $W(CO)_5$		61.69 ± 1.16	12.89 ± 0.22	59.35 ± 1.16	−6.0 ± 4.2	61.15 ± 0.08

[a] Calculated at 298.15 K. [b] Parameters for Se inversion.

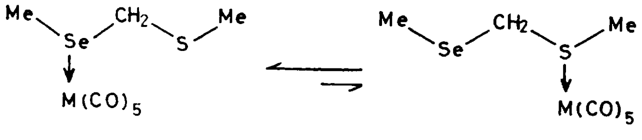

Figure 3. 1,3-Metal commutation in complexes $[M(CO)_5(MeSeCH_2SMe)]$ (M = Cr, Mo, or W)

Such equilibrations of methylene and both co-ordinated and unco-ordinated chalcogen methyl groups in two different linkage isomers and the absence of any exchange process with added free ligand indicate an intramolecular commutation of the $M(CO)_5$ moiety between the sulphur and selenium ligand atoms. The methylene region was chosen for complete bandshape fittings in all complexes, but the accuracy and consistency of this was checked by the fitting of a selection of spectra of the corresponding co-ordinated and unco-ordinated chalcogen methyl groups using the same rate constants for a given temperature. Static parameters used in the computation for all three complexes are given in Table 4, for the process illustrated in Figure 3. The experimental and best-fit computer-synthesized spectra of $[W(CO)_5(MeSeCH_2SMe)]$ in the methylene region are illustrated in Figure 2.

Discussion

Rate constants extracted from best-fit bandshapes of the spectra have been used to evaluate energy barriers. The Arrhenius and Eyring activation parameters for a pyramidal selenium inversion and the series of 1,3-metal commutations are summarized in Table 5. Discussions of the relative ease of fluxional processes in this section are based upon $\Delta G^\ddagger$ values (which are recognised as the least susceptible to systematic errors), at one standard temperature, 298.15 K.

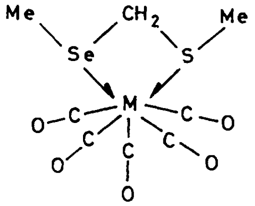

Figure 4. Proposed transition state in the 1,3-metal commutation process in the complexes $[M(CO)_5(MeSeCH_2SMe)]$ (M = Cr, Mo, or W)

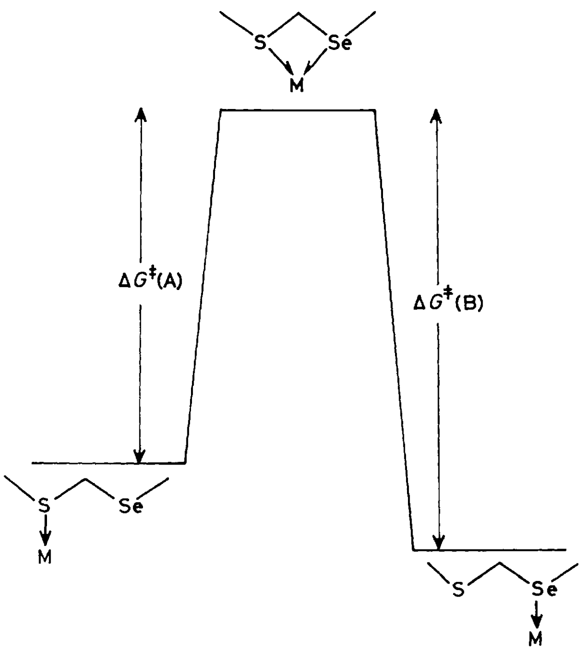

Figure 5. Energy profile for the 1,3-metal shifts illustrating the different values of $\Delta G^{\ddagger}$ for S→Se and Se→S commutations

Pyramidal Chalcogen Inversions.—Inversions about co-ordinated sulphur and selenium are observed for all complexes, with sulphur inversions having lower energy barriers than selenium. Low populations of the S-bonded isomers restrict a definitive series of experimental spectra suitable for full bandshape fitting, and a full analysis was carried out for the selenium inversion only in $[W(CO)_5(MeSeCH_2SMe)]$, as reported in Table 5. There are little data in the literature for comparison, but the $\Delta G^{\ddagger}$ value of 61.2 kJ mol^{-1} is similar to that of the analogous $[W(CO)_5(Me_3SiCH_2SeCH_2SiMe_3)]$ (58.5 kJ mol^{-1}).[11]

1,3-*Metal Commutations.*—The energy parameters for this novel heteronuclear commutation of the $M(CO)_5$ moiety between two co-ordination sites have been determined for all three complexes in both directions and are listed in Table 5.

A comparison of $\Delta G^{\ddagger}$ values reveals that the energy barrier for the Se→S 1,3-shift in the tungsten complex is *ca.* 10 kJ mol^{-1} higher than that for molybdenum. The same $\Delta G^{\ddagger}$ trend W > Cr > Mo was also observed for the S→Se 1,3-shift, but absolute values were lower by *ca.* 3—4 kJ mol^{-1}. This trend in the effect of the nature of the metal centre is comparable to that observed in 1,3-shifts in cyclic sulphur ligands,[3,4] and in the analogous 1,2-shifts in metal carbonyl complexes of disulphides and diselenides.[11]

These are the first observations of 1,3-metal commutations in dichalcogen metal complexes having two different co-ordination sites. In all cases the Arrhenius pre-exponential factors are close to 10^{13} s^{-1}; the process appears to have a rate independent of concentration and a total absence of exchange with added ligand, all three factors confirming the intramolecular nature of the process. The n.m.r. observations do not cast any light upon the detailed mechanism, but it is reasonable to propose a transition state in which the pentacarbonylmetal moiety is co-ordinately linked to the two different donor atoms simultaneously, as illustrated in Figure 4. Such a process would involve a pseudo-seven-co-ordinate state for the transition metal, and such higher co-ordination numbers are not unreasonable for Group 6 metal carbonyl derivatives.[12]

The energy profile for these commutations is illustrated in Figure 5 where the different free-energy changes $\Delta G^{\ddagger}(A)$ (S→Se) and $\Delta G^{\ddagger}(B)$ (Se→S) are due solely to the difference between the ground-state energies of the two isomers. This reflects quantitatively the stronger Se→M bond in these complexes, and $\Delta G^{\ddagger}(B) - \Delta G^{\ddagger}(A)$ might reasonably be regarded as reflecting the difference in the Se→M and S→M bond strength in these $M(CO)_5$ complexes: *ca.* 3.4 kJ mol^{-1} for $Cr(CO)_5$, *ca.* 3.9 kJ mol^{-1} for $Mo(CO)_5$, and *ca.* 2.9 kJ mol^{-1} for $W(CO)_5$.

Acknowledgements

We wish to thank the S.E.R.C. for use of the high-field n.m.r. spectroscopic service at the University of Warwick.

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Received 13*th May* 1986; *Paper* 6/912