

## Pyramidal Inversion and Novel 1,2-Metal Shifts in Pentacarbonyl-chromium, -molybdenum, and -tungsten Derivatives of Dialkyl Disulphides and Dialkyl Diselenides

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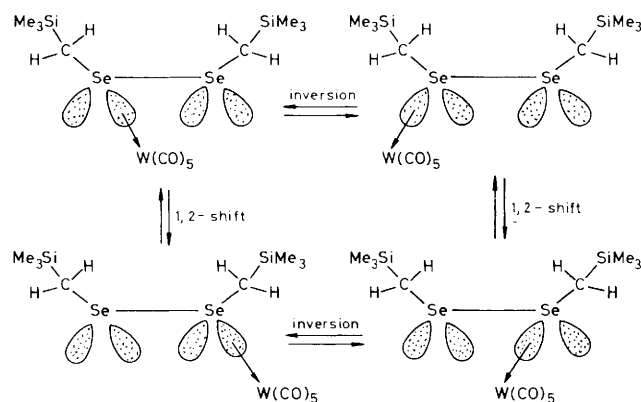
Variable temperature  $^1\text{H}$  n.m.r. spectroscopy of the mononuclear complexes  $[\text{M}(\text{CO})_5(\text{Me}_3\text{SiCH}_2\text{EECH}_2\text{SiMe}_3)]$ ,  $\text{M} = \text{Cr, Mo, and W}$ ,  $\text{E} = \text{S and Se}$ , establishes the occurrence of two distinct fluxional phenomena; the first is the not-unexpected pyramidal inversion about the co-ordinated sulphur or selenium atoms, but at higher temperatures a novel 1,2-metal shift between the two ligand atoms of the disulphide or diselenide occurs.

Sulphur and selenium complexes of the transition metals have shown themselves to be remarkable in the range of their fluxional phenomena,<sup>1</sup> and we report herein a new class of 1,2-metal shift. We have recently reported<sup>2</sup> the extensive characterization of 1,3-metal shifts<sup>3</sup> where the ligand sulphur atoms were separated by a single methylene group in such complexes as  $[\text{M}(\text{CO})_5\text{L}]$ ,  $\text{M} = \text{Cr and W}$ ,  $\text{L} =$

$\text{SCH}_2\text{SCH}_2\text{CH}_2\text{CH}_2$ , and also the intermetallic switching of disulphides and diselenides in binuclear metal complexes.<sup>4</sup> In order to ascertain the possibility of a simple 1,2-metal shift between ligand atoms in a mononuclear complex we have prepared the six compounds  $[\text{M}(\text{CO})_5(\text{Me}_3\text{SiCH}_2\text{EECH}_2\text{SiMe}_3)]$ ,  $\text{M} = \text{Cr, Mo, and W}$ ,  $\text{E} = \text{S and Se}$ . Among the advantages

**Table 1.** Arrhenius and activation parameters for ligand atom inversion and 1,2-metal shift in  $[\text{W}(\text{CO})_5(\text{Me}_3\text{SiCH}_2\text{SeSeCH}_2\text{SiMe}_3)]$ .

Fluxion	$E_a$ / $\text{kJ mol}^{-1}$	$\log_{10} A$	$\Delta G^\ddagger$ $\text{kJ mol}^{-1}$	$\Delta H^\ddagger$ $\text{kJ mol}^{-1}$	$\Delta S^\ddagger$ $\text{J K}^{-1} \text{mol}^{-1}$
Inversion	$59.8 \pm 0.8$	$13.6 \pm 0.2$	$54.8 \pm 0.1$	$57.7 \pm 0.8$	$9.7 \pm 3.0$
1,2-Shift	$82.6 \pm 1.6$	$13.5 \pm 0.2$	$78.4 \pm 0.2$	$79.8 \pm 1.6$	$4.7 \pm 4.7$

**Scheme 1**

of these particular ligands are the potential presence of prochiral methylene groups and the excellent solubility properties conferred on their complexes by the trimethylsilylmethylene groups.<sup>5</sup> Syntheses were carried out by the action of the disulphide or diselenide ligand upon the appropriate metal pentacarbonyl tetrahydrofuran precursor.<sup>6</sup>

The  $^1\text{H}$  n.m.r. spectral variation with temperature is exemplified by the behaviour of  $[\text{W}(\text{CO})_5(\text{Me}_3\text{SiCH}_2\text{SeSeCH}_2\text{SiMe}_3)]$ . At  $-40^\circ\text{C}$  the two different trimethylsilyl groups are apparent, as are the two different methylene groups. As each methylene group is prochiral they both appear as AB quartets; on warming, these quartets individually coalesce to sharp singlets at *ca.*  $25^\circ\text{C}$ . These changes result from pyramidal inversion about the metal bonded selenium atom only, and are represented by the horizontal processes in Scheme 1.

A further rise in temperature brings about the collapse of

the two trimethylsilyl group resonances to a singlet and also the two methylene signals to a singlet. These observations correspond to the 1,2-metal shift process indicated by the vertical changes in Scheme 1.

Computer-simulated line-shape fittings over a range of temperatures for both processes yield the Arrhenius and activation parameters indicated in Table 1. Corresponding  $\Delta G^\ddagger$  values for the 1,2-metal shifts in the sulphur compounds are 4–5  $\text{kJ mol}^{-1}$  lower than those of selenium; for the selenium and sulphur compounds, metal variation produces values for  $\Delta G^\ddagger$  in the order  $\text{W} > \text{Cr} > \text{Mo}$  for both the pyramidal inversion and the 1,2-metal shift processes.

The intramolecular nature of both fluxions indicated by the data in Table 1 is confirmed by the complete absence of exchange with added free ligand over the entire temperature range studied.

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