

1,3-Intramolecular Metal Shifts in Pentacarbonyltungsten(0) Complexes of 2,4-Dithiapentane, 2,4-Diselenapentane, and 2-Selena-4-thiapentane

Edward W. Abel, Suresh K. Bhargava, Thomas E. MacKenzie, Pramod K. Mittal, Keith G. Orrell, and Vladimir Šik

Department of Chemistry, The University, Exeter EX4 4QD, U.K.

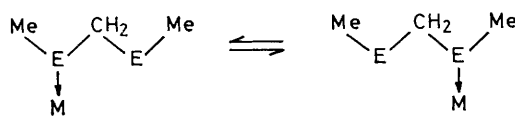
The mononuclear complexes $W(CO)_5L$ ($L = MeSCH_2SMe$, $MeSeCH_2SeMe$, and $MeSCH_2SeMe$) possess a novel fluxional character which from dynamic n.m.r. studies may be interpreted as intramolecular 1,3-metal jumps between ligand atoms; an indication of the relative strengths of the $S \rightarrow W$ and $Se \rightarrow W$ bonds is obtained from these studies.

Many different fluxional phenomena in sulphur and selenium metal complexes have been reported; in particular, 1,3-metal shifts have been observed¹ and characterised² in cyclic polythioethers. Recently 1,2-metal shifts have been observed³ in disulphides and diselenides, and we now report the analogous 1,3-metal shifts in pentacarbonyltungsten(0) complexes of acyclic dithio-, diseleno-, and selenothio-ethers.

The complexes were synthesised by the reaction of the ligand with either $[W(CO)_5(thf)]$ or $[W(CO)_5Br]^-$ (thf = tetrahydrofuran). The reaction with the selenothioether gave a mixture of the two isomers with selenium-tungsten and sulphur-tungsten bonds, respectively. The close correlations of the MeS and MeSe chemical shift data (Table 1) for all three complexes suggest the virtually identical bonding

Table 1. ^1H N.m.r. data for the complexes $[\text{W}(\text{CO})_5\text{MeECH}_2\text{E}'\text{Me}]$, $\text{E} = \text{S}$ or Se , $\text{E}' = \text{S}$ or Se , and ΔG^\ddagger values for the 1,3-metal shifts in these complexes.

Compound	$\delta/\text{p.p.m. (in CDCl}_3)$					ΔG^\ddagger (298.15 K)/ kJ mol^{-1}
	MeS \rightarrow W	MeS	MeSe \rightarrow W	MeSe	CH_2	
$[\text{W}(\text{CO})_5(\text{MeSCH}_2\text{SMe})]$	2.72	2.27			3.83	84.65 ± 0.66
$[\text{W}(\text{CO})_5(\text{MeSeCH}_2\text{SeMe})]$			2.62	2.16	3.98	85.82 ± 0.49
$[\text{W}(\text{CO})_5(\text{MeSeCH}_2\text{SMe})]$ (S \rightarrow W bonded)	2.72			2.19	3.83	83.36 ± 0.50 (S \rightarrow Se)
$[\text{W}(\text{CO})_5(\text{MeSeCH}_2\text{SeMe})]$ (Se \rightarrow W bonded)		2.25	2.60		3.85	86.30 ± 0.40 (Se \rightarrow S)



(E = S or Se)

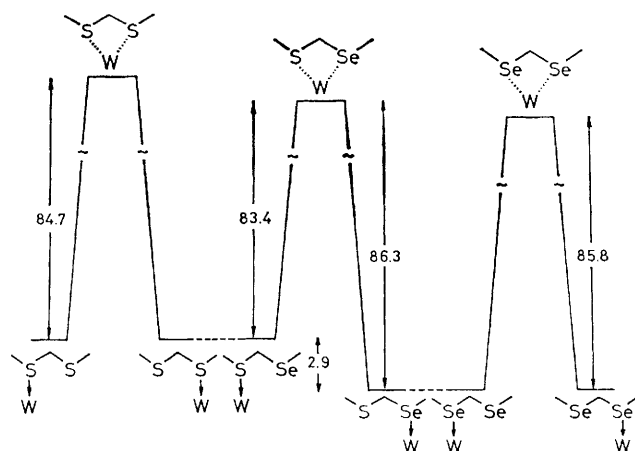
characteristics of the S \rightarrow W bonds in both $[\text{W}(\text{CO})_5(\text{MeSCH}_2\text{SeMe})]$ and $[\text{W}(\text{CO})_5(\text{MeSCH}_2\text{SMe})]$, and similarly for the nature of the Se \rightarrow W bonds in $[\text{W}(\text{CO})_5(\text{MeSCH}_2\text{SeMe})]$ and $[\text{W}(\text{CO})_5(\text{MeSeCH}_2\text{SeMe})]$.

Raising the temperature from 25 to 120 $^\circ\text{C}$ caused extensive spectral changes for all three complexes.

In $[\text{W}(\text{CO})_5(\text{MeSCH}_2\text{SMe})]$ and $[\text{W}(\text{CO})_5(\text{MeSeCH}_2\text{SeMe})]$, respectively, the two methyl group signals collapsed and this is attributable to a 1,3-metal shift between ligand atoms.

In the spectrum of $[\text{W}(\text{CO})_5(\text{MeSCH}_2\text{SeMe})]$ (two isomers), the four methyl signals collapsed to two, and the two methylene signals merged. The intramolecular nature of the process producing these changes was confirmed by a complete absence of exchange with added free ligand. Comparisons of experimental and computer-simulated spectra⁴ yielded rates of 1,3-shifts at temperatures within the n.m.r. dynamic range. Rate and temperature data were plotted according to the Arrhenius and Eyring equations, using least-squares fitting. Since ΔG^\ddagger values are the least susceptible of the activation parameters to temperature and rate errors,⁵ we have reported values for ΔG^\ddagger (298.15 K) in Table 1 as being most reliable.

Assuming a seven-coordinate transition state for these 1,3-metal shifts, the energy profile for these commutations is illustrated in Figure 1. We see that the selenium-to-selenium jump has a higher activation energy than the corresponding sulphur-sulphur movement, consistent with the same trend³ in analogous 1,2-shifts. From the difference between Se \rightarrow S and S \rightarrow Se 1,3-shift activation energies, it is possible to assess the difference between the ground state energies of the

**Figure 1.** Energy profile for 1,3-metal shifts showing ΔG^\ddagger (298.15 K) values (in kJ mol^{-1}) for the process and illustrating the difference in ground state energies for the isomers in $[\text{W}(\text{CO})_5(\text{MeSCH}_2\text{SeMe})]$.

Se-co-ordinated and S-co-ordinated isomers. This 2.9 kJ mol^{-1} difference reflects quantitatively the stronger Se \rightarrow W bond.

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