Rhenium and Manganese Carbonyl Difluorosulphoximides

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Summary Silver difluorosulphoximide and rhenium pentacarbonyl bromide react to give $Re(CO)_5NSOF_2$; heating of the product to 90 °C yields the dimeric species $[Re(CO)_4NSOF_2]_2$, with bridging $NSOF_2$-groups; with $Mn(CO)_5Br$, only the dimer was isolated.

THE first transition metal sulphur–nitrogen–fluorine compounds were recently prepared by the reaction of $AgN(SO_2F)_2$[1] with transition metal halides.[2] In the same way $AgNSOF_2$[3] introduces the difluorosulphoximide group [equation (1)]. $Re(CO)_5NSOF_2$ is a colourless solid,

$$\mathrm{Re(CO)_5Br + AgNSOF_2 \xrightarrow[\text{room temp.}]{CH_2Cl_2} Re(CO)_5NSOF_2 + AgBr\ (80\%)} \qquad (1)$$

m.p. 69—70°C, soluble in CH_2Cl_2, almost insoluble in non-polar organic solvents. As expected for C_{4v} symmetry three absorptions are found in the i.r. spectrum [A_1 2159 (w), E 2049 (vs), A_1 1996 (s) cm^{-1}] and three in the Raman spectrum [A_1 2160 (s), B_1 2085 (vs), A_1 1989 (s) cm^{-1}]. Bands due to the $-NSOF_2$ group are at 1461 (m) ($\nu_{as\ NSO}$), 1212 (m) ($\nu_{sym\ NSO}$), and 743 (s), 718 (s) ($\nu_{as\ SF}$, $\nu_{sym\ SF}$). The compound was further characterized by elemental analysis, mass spectroscopy [m/e 425/427 M^+, 397/399 $(M - CO)^+$], and ^{19}F n.m.r. (δ_{SF} $-60{\cdot}3$ p.p.m.).

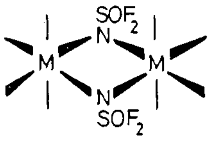
On heating to 90 °C in n-heptane, CO is evolved [equation (2)]. With $Mn(CO)_5Br$ this decomposition already takes place below

$$\mathrm{2Re(CO)_5NSOF_2 \xrightarrow[\text{n-heptane}]{90^{\circ}C} [Re(CO)_4NSOF_2]_2 + 2CO} \qquad (2)$$

room temperature [equation (3)].

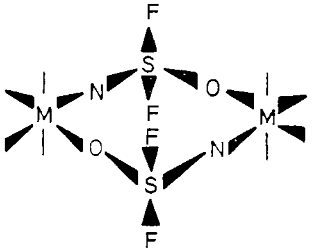
$$\mathrm{2Mn(CO)_5Br + 2AgNSOF_2 \xrightarrow[\text{room temp,}]{CH_2Cl_2} \{2[Mn(CO)_5NSOF_2] + 2AgBr\} \xrightarrow{-2CO} [Mn(CO)_4NSOF_2]_2\ (75\%)} \qquad (3)$$

The dimeric nature of the tetracarbonyls was shown for the rhenium derivative by mass spectroscopy [m/e 794, 796, 798 M^+; 766, 768, 770 $(M - CO)^+$; 738, 740, 742 $(M - 2CO)^+$]. The compounds are sparingly soluble in organic solvents; thermal decomposition occurs above 130°C (Mn) and 150°C (Re). The i.r. spectra of the solids are rather complex in the CO-stretching region, presumably due to site effects. {$[Re(CO)_4NSOF_2]_2$: 2117 (m), 2026 (s), 1995 (vs), 1974 (sh), 1960 (vs) ν_{CO}; 1395 (s), $\nu_{as\ NSO}$; 1205 (s), $\nu_{sym\ NSO}$, 791 (s) cm^{-1}, ν_{SF}. $[Mn(CO)_4NSOF_2]_2$: 2112 (m), 2040 (s), 2008 (vs), 1987 (sh), 1976 (vs), ν_{CO}; 1390 (s), $\nu_{as\ NSO}$, 1202 (s), $\nu_{sym\ NSO}$, 772 (s) cm^{-1}, ν_{SF}}. Because no CO-absorptions are found below 1900 cm^{-1}, the $NSOF_2$ group is thought to act as bridging species [(I) or (II)].



(I)

or



(II)

Comparing the geminal and the bridging $NSOF_2$ group, the largest shift is observed for $\nu_{as\ NSO}$ (mainly associated with a S-O stretching mode). This would favour structure (II).

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