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LETTER

S-Fluorosulfinato Rheniumpentacarbonyl

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A large number of transition metal sulfinato complexes (L_nMSO_2R) is described in the literature [1–3]. Linkage isomerism (S,O-coordination) is possible for the RSO_2 ligand, however low valent transition metals prefer to coordinate to the more polarizable sulfur donor atom. One general route to sulfinato complexes is the insertion of SO_2 into metal–alkyl or –aryl bonds. Detailed investigations of this insertion have shown, that the *O*-sulfinato complex might be formed initially as a kinetically favoured product, which rearranges to the thermodynamically more stable *S*-sulfinato derivative [4]. Several attempts to prepare organometallic *S*-fluorosulfinato complexes have failed; these compounds (e.g. derivatives of Pt or Mn) seemed to be unstable above –20 °C [5]. In contrast to these results, $Re(CO)_5SO_2F$ is stable at room temperature.

Experimental

A total of 0.92 g (1.59 mmol) $[Re(CO)_5SO_2]^+AsF_6^-$ (**2**) [6] and 1.00 g (3.60 mmol) TAS-fluoride [7, 8] are dissolved in 10 ml liquid SO_2 and stirred in a thick walled pressure vessel with a teflon valve at room temperature. After 1.5 h the volatile materials are removed under vacuum. A solid mixture of $TAS^+AsF_6^-$, $TAS^+SO_2F^-$ and $Re(CO)_5SO_2F$ (**3**) is left behind. The latter compound is very slightly soluble in methylene chloride and washing with this solvent gave analytically pure **3** as colorless residue (0.27 g, 42% yield), dec. > 140 °C.

Compound **3** is moderately soluble in SO_2, slightly soluble in acetone or acetonitrile and insoluble in petroleum ether or $CFCl_3$. IR (Nujol/KelF): 2170w, 2048(vs, broad), 1292m, 1138m, 650m, 567s, 530w cm^{-1}. ^{19}F NMR (SO_2/C_6D_6, $CFCl_3$ ext. stand.): $\delta = 93.5$ ppm. *Anal.* Found: C, 14.8; F, 4.7. Calc. for C_5FO_7ReS (409.3): C, 14.7; F, 4.6%.

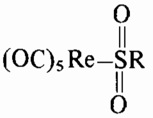
Results and Discussion

When dissolved in liquid SO_2, TAS-fluoride [tris(dimethylamino)sulfonium trimethyl difluorosilicoate, $(Me_2N)_3S^+Me_3SiF_2^-$)] immediately gives the corresponding fluorosulfinate derivative **1** [8], which reacts within seconds with the yellow **2** to give colorless $Re(CO)_5SO_2F$ (**3**).

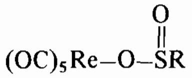
$$(Me_2N)_3S^+Me_3SiF_2^- + SO_2 \longrightarrow \underset{\mathbf{1}}{(Me_2N)_3S^+SO_2F^-} + Me_3SiF \qquad (1)$$

$$\mathbf{1} + \underset{\mathbf{2}}{[Re(CO)_5SO_2]^+AsF_6^-} \xrightarrow[-SO_2]{} \underset{\mathbf{3}}{Re(CO)_5SO_2F} + TAS^+AsF_6^- \qquad (2)$$

For **3**, the *S*-sulfinato structure A is suggested by comparison of its infrared spectrum with *O*- and *S*-methylsulfinato rheniumpentacarbonyl complexes [4, 9].

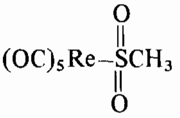

$$(OC)_5Re{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}R$$

A


$$(OC)_5Re{-}O{-}\overset{\overset{O}{\|}}{S}R$$

B**

In **3**, we assign the absorptions in the ν(CO) region to the A_1 and E/A_1 vibration modes of the pentacarbonyl group. As expected, when compared to


$$(OC)_5Re{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}CH_3$$

(ν(CO) = 2159w (A_1); 2053, 2050vs (E); 2018m (A_1) [9]), the upper A_1 mode is shifted to higher wave numbers while the broad unresolved E/lower A_1 modes are virtually unaffected. The isomeric methyl derivatives A and **B** have distinct differences in the SO stretching region (ν_{as}(SO) and ν_{sym}(SO) for A 1192 and 1054 cm^{-1}, for **B** 1126, 1106 and 818 cm^{-1}). In **3**, the SO stretches are observed at 1292 and 1138 cm^{-1}. These values are reasonable; when a methyl group is exchanged by a fluorine atom in the series, Me_2SO_2 [10], $MeSO_2F$ [11] and SO_2F_2

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***O,O*- and *S,O*-Sulfinates [1] seem unlikely.

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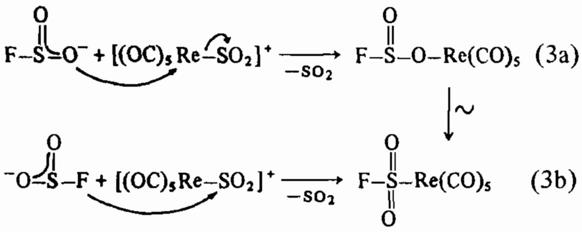
[12] the ν_{as}(SO) and ν_{sym}(SO) are shifted by about 75 and 50 cm^{-1}, respectively. The remaining bands in the IR spectrum of **3** (650m, 567s, 530w) are tentatively assigned to ν(SF), δ(ReCO) and δ(OSO).

In the ^{19}F NMR spectrum, the SF resonance of the SO_2F^- ion (103.3 ppm) [8] is shifted slightly to a higher field on coordination to the $Re(CO)_5$ group (δ = 93.5 ppm).

The mechanism for the formation of **3** is unresolved. There are two possible pathways:



The fluorosulfinate anion can attack the central rhenium and displace the SO_2 ligand in a nucleophilic fashion to give the *O*-sulfinate as a primary product. This subsequently rearranges to the thermodynamically more stable *S*-sulfinate. This pathway was suggested for the formation of the methyl derivative [4]. The second possibility (3b) is the fluoride ion transfer from the FSO_2^- anion to the coordinated SO_2 group. Further investigations will show if $TAS^+SO_2F^-$ offers a general method for the addition of fluoride to coordinated ligands.

Acknowledgements

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