Reactions of halides with *trans*-[Re(CO)$_4$(MeCN)(NS)][AsF$_6$]$_2$: syntheses and structures of *trans*-[Re(CO)$_4$Cl(NS)][AsF$_6$] and [(OC)$_5$ReN≡S–N=S–N[Re(CO)$_5$]S{=N–S≡NRe(CO)$_5$}–CH$_2$–CH$_2$][AsF$_6$]$_2$, an unusual trinuclear bis(thiazyl)rhenium complex

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From the reactions of *trans*-[Re(CO)$_4$(MeCN)(NS)][AsF$_6$]$_2$ with CsCl, *trans*-[Re(CO)$_4$Cl(NS)][AsF$_6$]·MeCN 2 is formed, and with CsF [{Re(CO)$_5$}$_3$(C$_2$H$_2$N$_5$S$_4$)][AsF$_6$]$_2$ 3 is isolated; the X-ray crystal structures of 2 and 3 are reported.

We have shown that halides exclusively add to the coordinated thionitrosyl ligand in [Re(CO)$_5$(NS)]$^{2+}$ yielding the corresponding thiazyl halide complexes [Re(CO)$_5$(NSX)]$^+$ (X = Cl, Br) in quantitative yield.[1] When the thionitrosyl dication is dissolved in acetonitrile, one of the carbonyl ligands is exchanged to give *trans*-[Re(CO)$_4$(MeCN)(NS)][AsF$_6$]$_2$ **1**.[2] Addition of halides to this system is rather complex, depending on the halides and on the counter ions, different results are obtained. With CsCl, exchange of the MeCN group is observed and [Re(CO)$_4$Cl(NS)][AsF$_6$]·MeCN **2** is isolated in 78% yield (Scheme 1).

The molecular structure of **2** is shown in Fig. 1.† Due to the heavy central metal atom, the standard deviations of the bond lengths are relatively high. Nevertheless, the short ReN distance documents the strong π-acceptor properties of the NS ligand.

trans-[Re(CO)$_4$(MeCN)(NS)][AsF$_6$]$_2$ + CsCl
1
↓
trans-[Re(CO)$_4$Cl(NS)][AsF$_6$]•MeCN
2
+ Cs[AsF$_6$]

Scheme 1

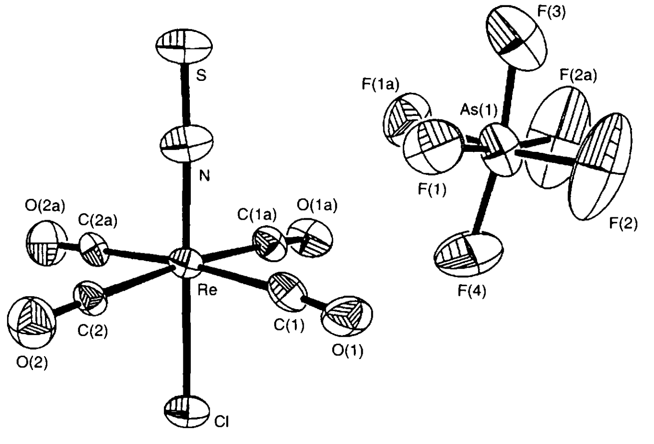
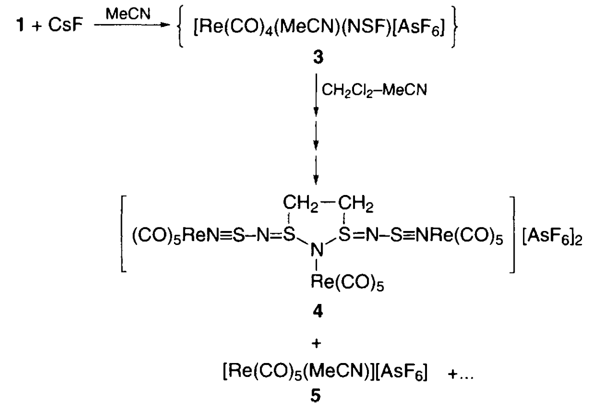


Fig. 1 Structure of **2** with 50% thermal ellipsoids; selected bond distances (pm) and bond angles (°): Re–N 187(2), Re–Cl 241.0(5), Re–C(av.) 202.6, N–S 145(2); Re–N–S 178(2), N–Re–Cl 179.2(7), N–Re–C(1) 91.8(6), N–Re–C(2) 94.3(6)

The influence on the NS bond length [145(2) pm] is small; a bond length of 142 pm is reported for the free NS$^+$ cation.[3] In accord with other thionitrosyl complexes the ReNS bond is linear [178(2)°].[4]

In contrast to the reaction with CsCl, in the reaction with CsF no products with Re–F bonds were isolated. ^{19}F NMR investigations of the primary product obtained at −10 °C from MeCN solution suggest the formation of *trans*-[Re(CO)$_4$-



$$1 + CsF \xrightarrow{MeCN} \{[Re(CO)_4(MeCN)(NSF)[AsF_6]\}\ \mathbf{3}$$

$$\downarrow CH_2Cl_2\text{–}MeCN$$

$$\left[(CO)_5ReN{\equiv}S\text{–}N{=}S(CH_2\text{–}CH_2)N(Re(CO)_5)S{=}N\text{–}S{\equiv}NRe(CO)_5\right][AsF_6]_2\ \mathbf{4}$$

$$+\ [Re(CO)_5(MeCN)][AsF_6]\ \mathbf{5}\ +\ldots$$

Scheme 2

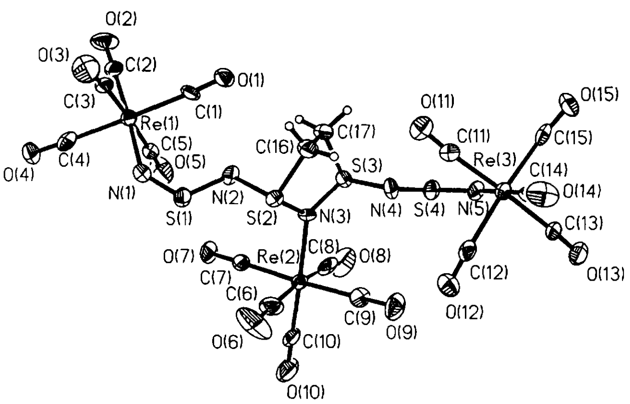
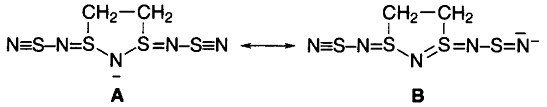


Fig. 2 Structure of the cation of **4** with 50% thermal ellipsoids; selected bond distances (pm) and bond angles (°): C(2)–Re(1) 196(1), Re(1)–N(1) 209(1), N(1)–S(1) 150(2), S(1)–N(2) 162(2), N(2)–S(2) 163(1), S(2)–N(3) 165(1), N(3)–S(3) 166(1), S(3)–N(4) 166(1), N(4)–S(4) 162(2), S(4)–N(5) 147(2), N(5)–Re(3) 213(1), Re(3)–C(14) 198(1), N(3)–Re(2) 220.5(9), Re(2)–C(10) 194(1), the average of all other Re–C distances is 201 ± 1, S(2)–C(16) 179(2), C(16)–C(17) 152(2), C(17)–S(3) 179(1); Re(1)–N(1)–S(1) 139(1) Re(3)–N(5)–S(4) 135.2(9), Re(2)–N(3)–S(2) 119.3(7), Re(2)–N(3)–S(3) 124.0(6), N(1)–S(1)–N(2) 113.6(7), N(5)–S(4)–N(4) 112.2(7), S(1)–N(2)–S(2) 112.2(7), S(4)–N(4)–S(3) 111.3(7), N(2)–S(2)–N(3) 106.8(6), N(4)–S(3)–N(3) 105.5(7), S(2)–N(3)–S(3) 116.6(5), C(16)–S(2)–N(3) 97.0(7), C(17)–S(3)–N(3) 95.7(7), S(2)–C(16)–C(17) 103(1), C(16)–C(17)–S(3) 106.8(9)



Scheme 3

(MeCN)(NSF)]AsF_6 **3**,[5] but attempts to recrystallise this compound from MeCN–CH_2Cl_2 led to extensive decomposition and exchange reactions‡ (Scheme 2).

Single crystals of **4** and **5** were isolated and characterised by X-ray crystallography.§ The structure of the cation of **4** is shown in Fig. 2.† The unusual trinuclear Re complex **4** contains an anionic tridentate ligand with two terminal thiazyl groups. According to the bond lengths observed, the bonding situation may be described best by valence structure **A** but **B** has also to be considered (Scheme 3).

The formation of this ligand cannot be explained easily. The sulfur–nitrogen chain originates from the thionitrosyl ligand, the CH_2–CH_2 bridge probably from the solvent mixture MeCN–CH_2Cl_2. The centre of this ligand is a $\overline{CH_2–CH_2–SNS}$ heterocycle. Such a ring system was also isolated as CH_2–CH_2–SNS–CH_2–CH_2^+ AsF_6^-[7] in the attempted recrystallisation of $[Re(CO)_5(NSBr)]^+[AsF_6]$ from MeCN–CH_2Cl_2 and unequivocally characterised by X-ray crystallography.¶

Footnotes

† *Crystal data*: for **2**; orthorhombic, space group *Cmca*, $a = 821.8(2)$, $b = 2576.3(5)$, $c = 1477.4(3)$ pm, $U = 3.1280(12)$ nm^3, $Z = 8$, $D_c = 2.589$ g cm^{-3}, $\mu = 10.25$ mm^{-1}, $F(000) = 2240$, crystal dimensions 0.6 × 0.2 × 0.05 mm. 5717 reflections collected with $2.5 < \theta < 27.5°$, 1908 unique ($R_{int} = 0.0416$) used in the structural analysis. The data set was collected on a Siemens P4 diffractometer using Mo-Kα radiation ($\lambda = 71.073$ pm) at 173 K. The structure was solved by direct methods. **2** crystalises with one solvent-molecule MeCN per formula unit. All atoms were refined anisotropically, the H atoms were ignored. An absorption correction was applied using the program DIFABS.[6] The refinement (117 parameters) converged to $wR = 0.0689$ and $R1 = 0.0579$ for 1160 observed reflections [$F > 6.0\sigma(F)$] and final difference electron density maxima, minima of 3060, −2160 e nm^{-3}.

For **4**; monoclinic, space group *Cc*, $a = 1465.8(3)$, $b = 2283.5(3)$, $c = 1316.8(3)$ pm, $\beta = 120.87(3)°$, $U = 3.7830(14)$ nm^3, $Z = 4$, $D_c = 2.779$ g cm^{-3}, $\mu = 11.65$ mm^{-1}, $F(000) = 2896$, crystal dimensions 0.4 × 0.3 × 0.05 mm. 9084 reflections collected with $2.5 < \theta < 27.5°$, 8183 unique ($R_{int} = 0.0147$) used in the structural analysis. Data collection and refinement as above. The refinement (523 parameters) converged to $wR = 0.0423$ and $R1 = 0.0396$ for 6659 observed reflections [$F < 4.0\sigma(F)$] and final difference electron density maxima, minima of 2970, −2540 e nm^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/26.

‡ From equimolar mixtures of CsF and **1** in MeCN at −10 °C a clear orange-red solution was formed within 30 min. After removal of the solvent under high vacuum, the residual solid was extracted with liquid SO_2. From this solution orange-red **3** (89%) was isolated. ^{19}F NMR (MeCN–CD_3CN–$CFCl_3$): δ +212 (s, SF), −63.9 [q, AsF, ^2J(AsF) 930 Hz]. IR (Nujol-KelF): 2938vw, 2311w, 2175w, 2062vs br, 704vs br. n-Pentane was slowly added to a solution of **3** in MeCN–CH_2Cl_2 at 0 °C by gas phase diffusion. After 2 days single crystals of **4** (orange-red) and **5** (colourless) were isolated.

§ **5** crystallises in the monoclinic space group *C2/m*. The cation and the anion are disordered.

¶ CH_2—CH_2–SNS–CH_2–CH_2^+ AsF_6^- was first prepared from NS_2^+ AsF_6^- in the presence of an excess of CH_2=CH_2 and characterised by X-ray crystallography.[7]

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