Activation of a ring methyl substituent in pentamethylcyclopentadienyl rhenium(v) compounds: synthesis and characterization of the 1,2,3,4-tetramethyl-5,6-dihydrofulvene-5,6-dithiolato complex $[ReO\{(S)(SCH_2)C_5Me_4\}(C_5Me_5)]$

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Reaction of the half-sandwich rhenium(v) complexes $[ReCl_4(C_5Me_5)]$ or $[Re(O)Cl_2(C_5Me_5)]$ with H_2S in chloroform in the presence of pyridine leads to the chiral dithiolato complex $[ReO\{(S)(SCH_2)C_5Me_4\}(C_5Me_5)]$ 1.

We have recently described[1–6] a number of sulfur-containing pentamethylcyclopentadienyl rhenium compounds, among them the mononuclear species $[Re(S_3)(S_4)(C_5Me_5)]$,[1] $[ReE(S_4)(C_5Me_5)]$ (E = O[1,2] or NBu^t[3]), $[Re(S_4)\{S_2C_2(CO_2Me)_2\}(C_5Me_5)]$,[4] $[Re(S_3)Cl_2(C_5Me_5)]$[3] and $[Re(CO)_2(S_2)(C_5Me_5)]$,[5] as well as the binuclear complexes $[Re_2(\mu\text{-}S_4)_2(C_5Me_5)_2]$,[1,2] $[Re_2O_2(\mu\text{-}S)(\mu\text{-}S_2)(C_5Me_5)_2]$,[2] $[Re_2(CO)_4(\mu\text{-}S)(C_5Me_5)_2]$[6] and $[Re_2(CO)_4(\mu\text{-}S_2)(C_5Me_5)_2]$.[5] All these compounds contain the C_5Me_5 ring ligand in the regular η^5-symmetrical coordination mode, as found in numerous other C_5Me_5 metal compounds involving sulfur ligands.[7]

We have now observed the unusual generation of a 5,6-dihydrofulvene-5,6-dithiolato ligand. If hydrogen sulfide gas is introduced into solutions containing either $[ReCl_4(C_5Me_5)]$[8] or $[Re(O)Cl_2(C_5Me_5)]$[8,9] in chloroform–pyridine (20 : 1) at room temperature, a red mononuclear (**1**) and a violet binuclear product (**2**)† can be isolated as main components of the reaction mixture [eqn. (1)].

$$3\,[Re(O)Cl_2(C_5Me_5)] + 8\,H_2S \xrightarrow[\substack{-2\,H_2O \\ -6\,HCl}]{CHCl_3}$$

$$\underset{\mathbf{1}}{[ReO\{(S)(SCH_2)C_5Me_4\}(C_5Me_5)]} + \underset{\mathbf{2}}{[Re_2S_6(C_5Me_5)_2]} \qquad (1)$$

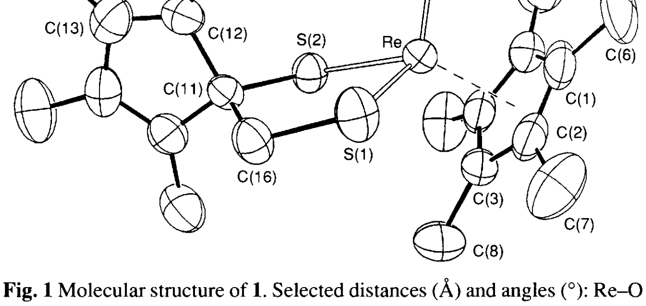

Fig. 1 Molecular structure of **1**. Selected distances (Å) and angles (°): Re–O 1.711(7), Re–S(1), 2.271(2), Re–S(2) 2.265(2); Re–C_5Me_5 (centroid) 2.013; Re–C(1) 2.394(7), Re–C(2) 2.336(7), Re–C(3) 2.326(8), Re–C(4) 2.321(7), Re–C(5) 2.376(7); S(1)–C(16) 1.837(6), S(2)–C(11) 1.886(6); C(11)–C(12) 1.523(11), C(11)–C(15) 1.507(8), C(11)–C(16) 1.508(9), C(12)–C(13) 1.337(9), C(13)–C(14) 1.462(12), C(14)–C(15) 1.358(10); S(1)–Re–S(2) 85.9(1), Re–S(1)–C(16) and Re–S(2)–C(11) 109.3(2).

The formation of the 5,6-dihydrofulvene-5,6-dithiolato complex **1** is tentatively explained by intermolecular interaction of an intermediate such as $[ReO(SH)_2(C_5Me_5)]$ or $[Re(O)S_2(C_5Me_5)]$ with a fulvene-type ligand. **1** is structurally related to the known benzene thiolato and ferrocene 1,1′-dithiolato analogues, $[ReO(SPh)_2(C_5Me_5)]$[10] and $[ReO\{(SC_5H_4)_2Fe\}(C_5Me_5)]$,[11] which can be obtained from $[Re(O)Cl_2(C_5Me_5)]$ and excess thiophenol or ferrocene 1,1′-dithiol, respectively. **2** has also been isolated, among other products, from the reaction of $[Re(O)Cl_2(C_5Me_5)]$ with $S(SiMe_3)_2$. The compositions of **1** and **2** are in agreement with analytical (C, H, S), ^1H and ^{13}C NMR as well as EI and FD mass spectroscopic data.

The molecular geometry of **1** has been determined by a single-crystal structure analysis (Fig. 1).‡ The 16-electron rhenium(v) complex contains a planar C_5Me_5 ring, an oxo ligand and the two sulfur atoms of the dithiolato ligand in a distorted tetrahedral (three-legged piano stool) arrangement. The dithiolato ring is bent along S(2)···O(16); the C(16)–S(1)–Re–S(2) plane includes dihedral angles with C_5Me_5 of 141.6° and with the S(2)–C(11)–C(16) plane of 147.3°. The diene ring C(11)–C(15) is planar and perpendicular to the S(2)–C(11)–C(16) plane (dihedral angle 89.5°). The Re–S bond lengths and S(1)–Re–S(2) angle in **1** (2.268 Å av., 85.9°) may be compared with the corresponding parameters in $[ReO(S_4)(C_5Me_5)]$ (2.254 Å av., 92.6°),[12] $[Re(S_3)(S_4)(C_5Me_5)]$ (2.373, 2.319 Å av., 89.6, 75.6°),[1] $[ReO(S_4)L]$ (2.281 Å av., 93.4°)[13] and $[ReO\{(SC_5H_4)_2Fe\}L]$ (2.313 Å av., 101.4°);[11] [L = hydrotris(3,5-dimethylpyrazol-1-yl)borate].

Although the insertion of oxygen into a metal–C_5Me_5 bond has been documented, *e.g.* in the formation of $[W(O)_2(\eta^1\text{-}OC_5Me_5)(C_5Me_5)]$ {from $[WO(C_5Me_5)_2]$ and O_2}[14,15] and $[VO(\mu\text{-}\eta^3\text{-}C_5Me_5O_3)]_2$ {by oxidation of $[V(C_5Me_5)_2]$ with O_2 at −78 °C},[16] the migration of a ring ligand to sulfur appears to be a less common reaction, an example being the intramolecular rearrangement of $[Ti(S_5)(C_5H_5)_2]$.[17] The ring-methyl C–H activation in C_5Me_5–metal complexes to give 1,2,3,4-tetramethylfulvene ligands is a matter of particular recent interest (*cf.* refs. 18–21 for examples and literature), and the bonding of 1,2,3,4-tetramethylfulvene in complexes such as $[M(\eta^6\text{-}Me_4C_5CH_2)(C_5Me_5)]BPh_4$ (M = Ru, Os)[22] and $[Ti(\eta^6\text{-}Me_4C_5CH_2)(C_5Me_5)]$[23] has been discussed.

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Footnotes

† *Characterization*: **1**, $[ReO\{(S)(SCH_2)C_5Me_4\}(C_5Me_5)]$ (dark-red solid, yield 25–30%); IR: ν(Re=O) 910 cm^{-1} (CsI); ^1H NMR (300 MHz, $CDCl_3$), δ 2.01 (s, 15 H, C_5Me_5), 1.56 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.73 (s, 3 H, CH_3), 2.00 (s, 3 H, CH_3), 2.74 [AB system, ^2J(HH) 14.0 Hz, 2 H, CH_2]. ^{13}C NMR (300 MHz, $CDCl_3$), δ 11.12 (C_5*Me*$_5$), 108.7 (*C*$_5$Me$_5$); 10.21,

10.76, 10.92 and 11.41 (four CH_3 substituents), 46.9 (CH_2S). EIMS (70 eV), *m/z* 536 (M^+, 20), 402 ($M^+ - CH_2C_5Me_4$, 24), 134 ($CH_2C_5Me_4$, 100), 119 ($C_5Me_5 - CH_4$, 100%).

2: [$Re_2S_6(C_5Me_5)_2$] (violet needles, yield 18–20%); ^{1}H NMR ($CDCl_3$), δ 2.25 (s, C_5Me_5); ^{13}C NMR ($CDCl_3$), δ 12.25 ($C_5\mathit{Me}_5$), 99.7 (C_5Me_5); EIMS (70 eV), *m/z* 836 (M^+, 4), 804 ($M^+ - S$, 10), 772 ($M^+ - 2S$, 100), 740 ($M^+ - 3S$, 30), 708 ($M^+ - 4S$, 23), 637 ($M^+ - 2S - C_5Me_5$, 14), 386 ($(M - 2S)^{2+}$, 20%); FDMS: *m/z* 836.5 (M^+).

‡ *Crystal data* for **1**: red plate, 0.08 × 0.22 × 0.45 mm, monoclinic, space group $C2/c$, a = 33.416(11), b = 9.054(4), c = 14.940(4) Å, β = 113.90(2)°, U = 4132.3(27) Å^3, Z = 8, D_c = 1.722 g cm^{-3}, μ = 6.088 mm^{-1}, $F(000)$ = 2112. Siemens P4 diffractometer, Mo-Kα radiation (λ = 0.710 73 Å), 298 K, 2θ range 4.0–55.0°, index ranges $-43 \leqslant h \leqslant 39$, $0 \leqslant k \leqslant 11$, $0 \leqslant l \leqslant 19$; 4715 reflections collected, 4546 independent (R_{int} = 3.20%), 3297 observed [$F > 5.0\sigma(F)$], 218 refined parameters. Siemens SHELXTL PLUS, direct methods. Final R indices (observed data), R = 0.0325, wR = 0.0400 [$w^{-1} = \sigma^2(F) + 0.0008F^2$], goodness-of-fit 0.97; max., min. residual electron density 0.95, −0.86 e Å^{-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 182/291.

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