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# Syntheses and reactivity of 'sulfur rich' Re(III) and Tc(III) complexes containing trithioperoxybenzoate, dithiobenzoate and dithiocarbamate ligands

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Reduction–substitution reactions of  $[M(O)Cl_4]^-$  (M = Re, <sup>99</sup>Tc) precursors with an excess of substituted dithiobenzoate ligands (R-PhCS<sub>2</sub>)<sup>-</sup> in dichloromethane/methanol mixtures afford a series of six-coordinated neutral mixed-ligand complexes of the type M<sup>III</sup>(R-PhCS<sub>3</sub>)<sub>2</sub>(R-PhCS<sub>2</sub>) (M = Re; **Re1–9**; M = <sup>99</sup>Tc; **Tc1–9**). The coordination sphere is entirely filled by sulfur donor atoms, and the complexes adopt a distorted trigonal prismatic arrangement, as assessed by the X-ray crystal structure analysis of Re(4-Me-PhCS<sub>3</sub>)<sub>2</sub>(4-Me-PhCS<sub>2</sub>), **Re2**. These compounds show sharp proton and carbon NMR profiles, in agreement with the diamagnetism typical of low spin d<sup>4</sup> trigonal prismatic configurations. The red-ox processes involve reduction of the metal from Re(v) to Re(III) and oxidation of dithiobenzoate to trithioperoxybenzoate. **M2–9** complexes contain a substitution-inert [M(R-PhCS<sub>3</sub>)<sub>2</sub>]<sup>+</sup> moiety including the metal and two trithioperoxybenzoate fragments, while the third dithiobenzoate ligand is labile. The latter is efficiently replaced by reaction with better nucleophiles such as diethyldithiocarbamate giving a further class of mixed ligand complexes of the type M<sup>III</sup>(R-PhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) (M = Re; **Re10–18**; M = <sup>99</sup>Tc; **Tc10–18**), which retain the trigonal prismatic arrangement, as determined by the X-ray analyses of the representative compounds Re(PhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>), **Re10** and <sup>99</sup>Tc(PhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>), **Tc10**.

## Introduction

<sup>188</sup>Re ( $t_1 = 17$  h;  $E_{\beta max} = 2.1$  MeV) offers advantageous nuclear properties for targeted radiotherapy.<sup>1</sup> The chemical similarity with its second-row congener technetium<sup>2</sup> allows one to take advantage of the huge efforts made in the last two decades in diagnosis with <sup>99m</sup>Tc, and to try to transfer this knowledge straight to rhenium based therapeutic analogues. In this connection, a step ahead has been recently provided by the introduction of <sup>188</sup>W/<sup>188</sup>Re generators,<sup>3</sup> theoretically identical to the widely used <sup>99</sup>Mo/<sup>99m</sup>Tc generators, which ensure the availability of carrier free amounts of [<sup>188</sup>ReO<sub>4</sub>]<sup>-</sup> for research purposes and preliminary phases of clinical trials.

Most of the rhenium based therapeutic agents proposed so far comprise the monooxo-Re(v) core surrounded by a series of tetra-dentate ligands including  $N_2S_2$ -diamino-dithiolate,  $N_2S_2$ diamido-dithiolate,  $N_3S$ -triamido-monothiolate frameworks, or by bis-bidentate  $S_2$ -dimercaptosuccinate chelates.<sup>1,4,5</sup> More recently, examples of low valent Re(I) species based on the organometallic [<sup>188</sup>Re(CO)<sub>3</sub>]<sup>+</sup> moiety and bifunctional ligand systems comprising bis[imidazol-2-yl]methylamine or iminodiacetic acid conjugates have been proposed for the labelling of biomolecules with high specific activity.<sup>6</sup>

In this context, much less explored so far is the possibility of stabilising <sup>188</sup>Re agents having the metal in intermediate oxidation states. Only very recently, sulfur donor ligands including tris(2-mercaptoethyl)amine<sup>7</sup> or dithiobenzoates<sup>8</sup> have proven to be efficient chelates to seek Re(III) and Tc(III) ions. The former tripodal ligand is utilised in conjunction with isocyanides or monophosphines to stabilise the so called '4 + 1' system in a trigonal bipyramidal arrangement,<sup>7</sup> and dithiobenzoates (PhCS<sub>2</sub>)<sup>-</sup> give unexpected mixed ligand complexes after metal induced oxidation of the ligand and formation of sulfur enriched trithioperoxybenzoate (PhCS<sub>3</sub>)<sup>-</sup> adducts. The resulting sixcoordinated neutral compound M(PhCS<sub>3</sub>)<sub>2</sub>(PhCS<sub>2</sub>) contain two oxidised dithiobenzoate and one dithiobenzoate unit.<sup>8,9</sup>

Preparation of the above mentioned 'sulfur rich' complexes at carrier free level starting from generator eluted [99mTcO4] and [188 ReO<sub>4</sub>]- confirmed the possibility of stabilising M(III) ions in extremely dilute conditions.<sup>10</sup> The concomitant presence of several sulfur atoms and phenyl groups imparts a lipophilic character to these molecules, a property which can be profitably used for applications in nuclear medicine. For example,  $M(PhCS_3)_2(PhCS_2)$  (M = <sup>99m</sup>Tc, <sup>188</sup>Re) was recently investigated for the treatment of hepatocellular carcinoma in animal models. Indeed, this 'sulfur rich' radiopharmaceutical is able to label efficiently lipiodol, and the resulting mixture has shown elevated uptake and retention in the hepatic tissue of animal models.<sup>11</sup> Moreover, with the aim of finding suitable radiopharmaceuticals in the differentiation of infection versus inflammation, 99m Tc(PhCS3)2(PhCS2) complexes have shown high yield and selective in vitro labelling of lymphocytes in whole blood.12

The promising biological properties of M(PhCS<sub>3</sub>)<sub>2</sub>(PhCS<sub>2</sub>) agents prompted us to prepare a series of related M(III) complexes to validate the surprising synthetic pathway which resulted in the mixed bis-trithioperoxybenzoate dithiobenzoato coordination sphere. In addition, possible fine tuning of the lipophilic–hydrophilic balance of the resulting complexes might eventually improve their biological properties. Hence, we have prepared a series of substituted dithiobenzoato compounds of general formula M(R-PhCS<sub>3</sub>)<sub>2</sub>(R-PhCS<sub>2</sub>), **M2–9**, and characterised them both in the solid state and in solution by conventional physicochemical techniques. All of these compounds,

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including the unsubstituted analogs M(PhCS<sub>3</sub>)<sub>2</sub>(PhCS<sub>2</sub>), M1, undergo substitution of the unique dithiobenzoate for dithiocarbamate without affecting the geometry of the substitution-inert  $[M(R-PhCS_3)_2]^+$  moieties. Hence, an additional series of mixed bis-trithioperoxybenzoate dithiocarbamate complexes M(R-PhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>), M10–18, have been prepared and X-ray authenticated. The effect of the various substituents incorporated in the aromatic ring has been analysed by means of several techniques including cyclovoltammetry, UV-vis and NMR spectroscopy. Kinetic and thermodynamic stability measurements in biological media of selected compounds are in progress.

# Experimental

**CAUTION**! <sup>99</sup>Tc is a weak  $\beta$ -emitter ( $E_{\beta} = 0.292$  MeV,  $t_{1/2} =$  $2.12 \times 10^5$  years). All manipulations were carried out in laboratories approved for low-level radioactivity using monitored hoods and glove-boxes. When handled in milligram amounts, <sup>99</sup>Tc does not present a serious health hazard since common laboratory glassware provides adequate shielding. Bremsstrahlung is not a significant problem due to the low-energy of the  $\beta$ particles. However, normal radiation safety procedures must be used at all times, especially with solid samples, to prevent contamination and inhalation.

Dichloromethane and petroleum ether (PE) (bp 30-60 °C) were purified according to the methods reported in the literature.13 Methanol was used as received. Diethyldithiocarbamate sodium salt (Nadedc) was purchased from Aldrich (Saint Quentin Fallavier, France). Dithiobenzoate sodium (Nadtb) or piperidinium (Pipdtb) salts were prepared as described previously.14 [ReOCl4][NBu4]15 and [99TcOCl4][NBu4]16 were synthesised according to literature methods.

Carbon, hydrogen and oxygen analysis were performed by I.C.S.N. (Gif sur Yvette, France) on a Carlo Erba elemental analyser Model-1106 or by C.R.M.P.O (Rennes, France) on a ThermoFinnigan elemental analyser Flash EA1112 CHNS/O. FT IR spectra were recorded on a Nicolet 510P Fourier-transform spectrometer in the range 4000-400 cm<sup>-1</sup> in KBr mixtures using a Spectra-Tech diffuse-reflectance collector accessory for technetium compounds or on a Mattson 3030 Fourier-transform spectrometer in the range 4000-400 cm<sup>-1</sup> in KBr pellets for rhenium compounds. <sup>1</sup>H and <sup>13</sup>C NMR spectra were collected in CDCl<sub>3</sub> on a BRUKER ARX 400 (rhenium compounds) and on a BRUKER AC 300 (technetium compounds), using SiMe<sub>4</sub> as internal reference. Cyclic voltammetry measurements were performed on a BAS (Bioanalytical System Inc.) CV-1B cyclic voltammograph at 293 K under an atmosphere of nitrogen by using a conventional three-electrode cell. A platinum-disk electrode (area  $ca. 10^{-3} \text{ cm}^2$ ) was used as the working electrode, a platinum wire as the counter electrode, and a silver wire as a quasi-reference electrode. Controlled potential coulometries were performed using an Amel model 721 integrator, in an H-shaped cell containing, in arm 1, a platinum gauze working electrode and an Ag/Ag<sup>+</sup> reference isolated inside a salt bridge by a medium-glass frit and, in arm 2, an auxiliary platinum-foil electrode. The UV-Vis spectra were recorded in dichloromethane on a Spectronic Unicam UV500 UV-Visible spectrometer equipped with Vision 32 software. Spectra were recorded in the region from 190 to 780 nm using  $10^{-4}$  to  $10^{-6}$  M solutions. The magnitude of the absorption coefficients was between 103 and 105 cm<sup>-1</sup> M<sup>-1</sup>. UV-vis data of bis-trithioperoxybenzoate dithiobenzoate complexes have been analysed in detail in a separate contribution.<sup>17</sup> Thin layer chromatography was performed on silica gel F<sub>254S</sub> plates (Merck).

#### Synthesis of rhenium complexes

Bis-trithioperoxybenzoato dithiobenzoato complexes Re(R- $PhCS_3)_2(R-PhCS_2)$  were synthesised according to the procedure utilised for the unsubstituted complex with R = H (Re1).<sup>8</sup>

**Re(4-MePhCS<sub>3</sub>)<sub>2</sub>(4-MePhCS<sub>2</sub>) (Re2).** Yield 53% (0.068 g). Elemental analysis: molecular formula C<sub>24</sub>H<sub>21</sub>S<sub>8</sub>Re. Found: %C = 38.83, %H = 2.76, %S = 34.05; Calc. for [Re(4- $MePhCS_{3}(4-MePhCS_{2})$ ]: %C = 38.33, %H = 2.81, %S = 34.10.  $Mp = 168 \degree C. R_f (PE/CH_2Cl_2 7/3) = 0.79. IR (KBr disk) (cm^{-1}):$ 1598 (s), 1501 (w), 1408 (w), 1309 (m), 1262 (s), 1220 (w), 1179 (s), 1096 (s), 1015 (s, v<sub>C-s</sub>), 950 (m), 910 (w), 879 (w), 812 (s), 706 (w), 544 (m, v<sub>s-s</sub>), 447 (m), 399 (m, v<sub>Re-s</sub>). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  2.42 (s, 3H, CH<sub>3</sub>), 2.59 (s, 6H, CH<sub>3</sub>), 7.15 (d, J = 8.4 Hz, 2H, H<sub>aromatic</sub>), 7.30 (d, J = 8.4 Hz, 4H, H<sub>aromatic</sub>), 7.59 (d, J = 8.1 Hz, 2H, H<sub>aromatic</sub>), 7.94 (d, J = 8.1 Hz, 4H,  $H_{aromatic}$ ). <sup>13</sup>C NMR (100.67 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{C}$  21.6 and 30.10 (OCH<sub>3</sub>), 125.2 128.6 129.3 and 132.3 (CH<sub>aromatic</sub>), 133.0 and 141.2 (C-CH<sub>3</sub>), 144.5 (C-CS<sub>3</sub>), 144.9 (C-CS<sub>2</sub>), 234.2 (CS<sub>3</sub>), 238.6 (CS<sub>2</sub>).

Re(4-EtPhCS<sub>3</sub>)<sub>2</sub>(4-EtPhCS<sub>2</sub>) (Re3). Yield 70% (0.095 g). Elemental analysis: molecular formula  $C_{27}H_{27}S_8Re$ . Found: %C = 40.83, %H = 3.43, %S = 32.05; Calc. for [Re(4-EtPhCS<sub>3</sub>)<sub>2</sub>(4- $EtPhCS_2$ ]: %C = 40.84, %H = 3.43, %S = 32.30. Mp = 164 °C.  $R_{\rm f}$  (PE/CH<sub>2</sub>Cl<sub>2</sub>7/3) = 0.76. IR (KBr disk) (cm<sup>-1</sup>): 1595 (s), 1449 (w), 1413 (w), 1273 (m), 1240 (s), 1179 (s), 1054 (m), 1008 (s, v<sub>C-s</sub>), 964 (s), 905 (s), 832 (s), 768 (w), 593 (w), 561 (m,  $v_{s-s}$ ), 465 (w), 438 (w), 408 (w), 385 (m, v<sub>Re-S</sub>). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  1.20 (t, J = 7.6 Hz, 3H, CH<sub>3</sub>), 1.28 (t, J = 7.6 Hz, 6H, CH<sub>3</sub>), 2.70 (q, J = 7.4 Hz, 2H, CH<sub>2</sub>), 2.84 (q, J = 7.6 Hz, 4H, CH<sub>2</sub>), 7.18 (d, J = 8.4 Hz, 2H, H<sub>aromatic</sub>), 7.32 (d, J = 8.4 Hz, 4H,  $H_{aromatic}$ ), 7.61 (d, J = 8.4 Hz, 2H,  $H_{aromatic}$ ), 7.96 (d, J = 8.1 Hz, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (100.67 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  14.2 and 16.1 (CH<sub>3</sub>), 28.9 and 29.2 (CH<sub>2</sub>), 125.3 127.4 128.1 and 132.4 (CH<sub>aromatic</sub>), 133.2 141.4 150.7 and 151.0 (C<sub>aromatic</sub>), 234.2 (CS<sub>3</sub>), 238.5 (CS<sub>2</sub>).

Re(2-EtPhCS<sub>3</sub>)<sub>2</sub>(2-EtPhCS<sub>2</sub>) (Re4). Yield 62% (0.084 g). Elemental analysis: molecular formula  $C_{27}H_{27}S_8Re$ . Found: %C = 40.81, %H = 3.43, %S = 31.95; Calc. for [Re(2-EtPhCS<sub>3</sub>)<sub>2</sub>(2- $EtPhCS_2$ ]: %C = 40.84, %H = 3.43, %S = 32.30. Mp = 170 °C.  $R_{\rm f}$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.70. IR (KBr disk) (cm<sup>-1</sup>): 1476 (m), 1458 (m), 1441 (s), 1371 (w), 1259 (w), 1190 (w), 1160 (w), 1119 (w), 1057 (w), 1000 (s,  $v_{C-S}$ ), 943 (m), 913 (w), 751 (s), 544 (s,  $v_{s-s}$ ), 454 (m), 399 (m,  $v_{Re-s}$ ). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  1.19 (t, J = 7.5 Hz, 3H, CH<sub>3</sub>), 1.24 (t, J = 7.5 Hz,  $6H, CH_3$ , 2.77 (q, J = 7.6 Hz, 2H, CH<sub>2</sub>), 3.00 (q, J = 7.5 Hz, 4H, CH<sub>2</sub>), 7.19 (m, 2H, H<sub>aromatic</sub>), 7.25 (m, 2H, H<sub>aromatic</sub>), 7.36 (m, 4H, H<sub>aromatic</sub>), 7.44 (m, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (100.67 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  16.2 (CH<sub>3</sub>), 26.8 (CH<sub>2</sub>), 125.4 128.4 129.7 131.4 125.7 129.1 130.9 and 131.8 (CH<sub>aromatic</sub>), 134.0 141.7 143.9 and 145.5 (Caromatic), 235.4 (CS<sub>3</sub>), 243.9 (CS<sub>2</sub>).

Re(4-MeOPhCS<sub>3</sub>)<sub>2</sub>(4-MeOPhCS<sub>2</sub>) (Re5). Yield 54% (0.074 g). Elemental analysis: molecular formula  $C_{24}H_{21}O_3S_8Re$ . Found: %C = 36.03, %H = 2.64, %S = 31.96; Calc. for  $[Re(4-MeOPhCS_3)_2(4-MeOPhCS_2)]: \%C = 36.03, \%H = 2.65,$ %S = 32.06. Mp = 170 °C.  $R_f$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.25. IR (KBr disk) (cm<sup>-1</sup>): 1592 (s), 1564 (w), 1501 (m), 1452 (w), 1305 (m), 1259 (s), 1169 (s), 1116 (w), 1027 (s, v<sub>C-s</sub>), 992 (w), 948 (w), 912 (w), 883 (w), 827 (s), 805 (w), 733 (w), 631 (w), 593 (m,  $v_{s-s}$ ), 545 (w), 398 (m, v<sub>Re-S</sub>). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  3.83 (s, 3H, OCH<sub>3</sub>), 3.92 (s, 6H, OCH<sub>3</sub>), 6.84 (d, J = 8.9 Hz, 2H, H<sub>aromatic</sub>), 6.98 (d, J = 8.9 Hz, 4H, H<sub>aromatic</sub>), 7.67 (d, J =9.2 Hz, 2H,  $H_{aromatic}$ ), 8.06 (d, J = 6.7 Hz, 4H,  $H_{aromatic}$ ). <sup>13</sup>C NMR (100.67 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  55.9 and 56.0 (OCH<sub>3</sub>), 113.2 113.9 127.4 128.9 (CH<sub>aromatic</sub>), 134.2 (C-CS<sub>3</sub>), 137.6 (C-CS<sub>2</sub>), 164.5 and 165.0 (C-OCH<sub>3</sub>), 233.4 (CS<sub>3</sub>), 237.1 (CS<sub>2</sub>).

Re(3-MeOPhCS<sub>3</sub>)<sub>2</sub>(3-MeOPhCS<sub>2</sub>) (Re6). Yield 65% (0.089 g). Elemental analysis: molecular formula  $C_{24}H_{21}O_3S_8Re$ . Found: %C = 36.11, %H = 2.63, %S = 31.71; Calc. for  $[\text{Re}(3-\text{MeOPhCS}_3)_2(3-\text{MeOPhCS}_2)]: \%\text{C} = 36.03, \%\text{H} = 2.65,$ %S = 32.06. Mp = 178 °C.  $R_{\rm f}$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.19. IR (KBr disk) (cm<sup>-1</sup>): 1593 (w), 1570 (s), 1476 (m), 1425 (m), 1321 (w), 1286 (m), 1261 (s), 1200 (w), 1162 (w), 1098 (s), 1050 (s),

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1017 (s,  $v_{C-S}$ ), 978 (w), 948 (w), 866 (m), 803 (s), 678 (s), 564 (m,  $v_{S-S}$ ), 395 (m,  $v_{Re-S}$ ). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  3.79 (s, 3H, OCH<sub>3</sub>), 3.91 (s, 6H, OCH<sub>3</sub>), 6.91 (m, 3H, Haromatic), 7.20 (m, 1H, Haromatic), 7.29 (m, 3H, Haromatic), 7.41 (t, J = 7.9 Hz,1H, Haromatic), 7.58 (m,4H, Haromatic).<sup>13</sup>C NMR (100.67 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  55.8 and 56.0 (OCH<sub>3</sub>), 116.8 119.9 125.2 129.5 (CH<sub>aromatic</sub>), 136.4 (*C*-CS<sub>3</sub>), 144.4 (*C*-CS<sub>2</sub>), 159.0 and 159.4 (*C*-OCH<sub>3</sub>), 234.0 (CS<sub>3</sub>), 238.6 (CS<sub>2</sub>).

**Re(2-MeOPhCS<sub>3</sub>)<sub>2</sub>(2-MeOPhCS<sub>2</sub>)** (Re7). Yield 59% (0.080 g). Elemental analysis: molecular formula  $C_{24}H_{21}O_3S_8Re$ . Found: %C = 36.10, %H = 2.59, %S = 32.00; Calc. for  $[Re(2-MeOPhCS_3)_2(2-MeOPhCS_2)]: \%C = 36.03, \%H = 2.65,$ %S = 32.06. Mp = 180 °C.  $R_f$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.22. IR (KBr disk) (cm<sup>-1</sup>): 1589 (m), 1568 (w), 1480 (s), 1458 (s), 1429 (m), 1284 (m), 1250 (s), 1164 (m), 1097 (s), 1047 (w), 1012 (s,  $v_{C-S}$ ), 944 (w), 913 (w), 878 (w), 801 (s), 752 (s), 648 (w), 568 (w,  $v_{s-s}$ ), 383 (w,  $v_{Re-s}$ ). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{H}$ 3.84 (s, 3H,  $OCH_3$ ), 3.93 (s, 6H,  $OCH_3$ ), 6.88 (d, J = 8.4 Hz, 1H,  $H_{aromatic}$ ), 6.95 (t, J = 7.1 Hz, 1H,  $H_{aromatic}$ ), 7.11 (m, 4H,  $H_{aromatic}$ ), 7.22 (d, J = 7.1 Hz, 1H,  $H_{aromatic}$ ), 7.35 (t, J = 8.4 Hz, 2H,  $H_{aromatic}$ ), 7.79 (dd, J = 8.1 Hz and J = 1.8 Hz, 1H,  $H_{aromatic}$ ), 7.91 (dd, J = 7.6 Hz and J = 1.5 Hz, 2H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (100.67 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>): δ<sub>C</sub> 55.8 and 56.4 (OCH<sub>3</sub>), 111.2 111.9 119.7 120.9 126.1 128.6 (CH<sub>aromatic</sub>), 133.8 (C-CS<sub>3</sub>), 134.5 (C-CS<sub>2</sub>), 157.1 and 158.4 (C-OCH<sub>3</sub>), 229.4 (CS<sub>3</sub>), 234.6 (CS<sub>2</sub>).

**Re(4-FPhCS<sub>3</sub>)<sub>2</sub>(4-FPhCS<sub>2</sub>) (Re8).** Yield 77% (0.100 g). Elemental analysis: molecular formula  $C_{21}H_{12}F_3S_8Re$ . Found: %C = 33.12, %H = 1.63, %S = 30.70. Calc. for [Re(4-FPhCS<sub>3</sub>)<sub>2</sub>(4-FPhCS<sub>2</sub>)]: %C = 33.00, %H = 1.60, %S = 33.60. Mp = 120 °C. *R*<sub>f</sub> (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.67. IR (KBr disk) (cm<sup>-1</sup>): 1591 (m), 1499 (s), 1407 (w), 1304 (w), 1280 (w), 1265 (w), 1237 (s), 1156 (m), 1008 (s, *v*<sub>C-S</sub>), 1001 (s, *v*<sub>C-S</sub>), 834 (m), 807 (w), 578 (w), 547 (w), 547 (s, *v*<sub>S-S</sub>), 454 (m), 399 (m, *v*<sub>Re-S</sub>). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  7.00 (t, *J* = 8.6 Hz, 2H, H<sub>aromatic</sub>), 7.15 (t, *J* = 8.5 Hz, 4H, H<sub>aromatic</sub>), 7.64 (dd, *J* = 5.3 and 8.9 Hz, 2H, H<sub>aromatic</sub>), 8.00 (dd, *J* = 5.3 and 8.9 Hz, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (100.67 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  114.9 (d, *J* = 22.2 Hz, CH<sub>aromatic</sub>), 131.3 (*C*-CS<sub>3</sub>), 131.4 (*C*-CS<sub>2</sub>), 134.0 (d, *J* = 8.1 Hz, CH<sub>aromatic</sub>), 139.7, 142.0 142.2 and 142.5 (C–F), 232.6 (CS<sub>3</sub>), 244.4 (CS<sub>2</sub>).

**Re(3-FPhCS<sub>3</sub>)<sub>2</sub>(3-FPhCS<sub>2</sub>) (Re9).** Yield 48% (0.063 g). Elemental analysis: molecular formula  $C_{21}H_{12}F_3S_8$ Re. Found: %C = 33.01, %H = 1.58, %S = 30.57. Calc.for [Re(3-FPhCS<sub>3</sub>)<sub>2</sub>(3-FPhCS<sub>2</sub>)]: %C = 33.00, %H = 1.60, %S = 33.60. Mp = 125 °C.  $R_f$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.70. IR (KBr disk) (cm<sup>-1</sup>): 1581 (w), 1479 (m), 1433 (m), 1249 (s), 1158 (w), 1136 (w), 1026 (m,  $v_{C-8}$ ), 1001 (w), 963 (s), 869 (m), 824 (w), 809 (m), 786 (s), 690 (m), 672 (s), 563 (w,  $v_{S-8}$ ), 521 (w), 372 (w,  $v_{Re-5}$ ). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_H$  7.07 (td, J = 8.1 and 2,6 Hz, 3H, H<sub>aromatic</sub>), 7.36 (m, 2H, H<sub>aromatic</sub>), 7.49 (m, 3H, H<sub>aromatic</sub>), 7.80 (m, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (100.67 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_C$  115.3 122.0 and 124.4 (CH<sub>aromatic</sub>), 131.2 and 137.3 (*C*-CS<sub>2</sub>), 161.9 and 164.4 (*C*-F), 229.3 (CS<sub>3</sub>), 242.3 (CS<sub>2</sub>).

Bis-trithioperoxybenzoato diethyldithiocarbamato  $Re(R-PhCS_3)_2(Et_2NCS_2)$  were prepared as detailed below using two different procedures.

*Procedure (a).* To a CH<sub>2</sub>Cl<sub>2</sub> solution (5 mL) containing **Re1** (0.05 g, 0.070 mmol), diethyldithiocarbamate sodium salt (5 equivalents) dissolved in methanol (5 mL) was added dropwise and the solution stirred at room temperature for 2 h. The solvent was removed by evaporation under vacuum and the residue loaded onto a silica chromatography column and eluted with a mixture of petroleum ether and CH<sub>2</sub>Cl<sub>2</sub> (8 : 2, v/v). The browngreen band was collected, and, after removal of the solvent by evaporation under vacuum, an olive green solid was obtained: this powder was dissolved in a mixture of petroleum ether and CH<sub>2</sub>Cl<sub>2</sub> (1 : 1, v/v) and after 3 days, crystals were collected. *Procedure* (*b*). To a MeOH solution (5 mL) containing [ReOCl<sub>4</sub>][NBu<sub>4</sub>] (0.15 g, 0.265 mmol), the pertinent dithiobenzoate sodium salt (5 equivalents) and the diethyldithiocarbamate sodium salt (5 equivalents), in MeOH (5 mL) were added dropwise and the solution was stirred at room temperature for 2 h. The precipitate was filtered off, washed several times with MeOH or EtOH, loaded onto a silica chromatography column and eluted with a mixture of petroleum ether and CH<sub>2</sub>Cl<sub>2</sub> (8 : 2, v/v). The brown-green band was collected, and after removal of the solvent by evaporation under vacuum, an olive green solid was obtained: this powder was dissolved in a mixture of petroleum ether and CH<sub>2</sub>Cl<sub>2</sub> (1 : 1, v/v) and after 3 days, crystals were collected.

**Re(PhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) (Re10).** Procedure (a) yield 75% (0.090 g). Procedure (b) yield 50% (0.025 g). Elemental analysis: molecular formula C<sub>19</sub>H<sub>20</sub>NReS<sub>8</sub>. Found: %C = 32.44, %H = 2.87, %S = 36.41; Calc. for [Re(PhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>)]: %C = 32.35, %H = 2.86, %S = 36.36. Mp = 165 °C. *R*<sub>f</sub> (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.50. IR (KBr disk) (cm<sup>-1</sup>): 1504 (s), 1482 (m), 1454 (m), 1440 (s), 1377 (w), 1354 (w), 1300 (w), 1275 (m), 1241 (m), 1208 (m), 1179 (w), 1078 (w), 1028 (w), 1001 (s), 990 (s, *v*<sub>C-S</sub>), 908 (m), 755 (s), 687 (s), 544(s, *v*<sub>S-S</sub>), 454 (m), 399 (m, *v*<sub>R-S</sub>). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  1.19 (t, *J* = 7.1 Hz, 6H, CH<sub>3</sub>), 3.60 (m, 4H, CH<sub>2</sub>), 7.31 (t, *J* = 8.1 Hz, 2H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (100.67 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  12.8 (CH<sub>3</sub>), 44.4 (CH<sub>2</sub>), 128.1 132.4 and 132.8 (CH<sub>aromatic</sub>), 134.9 (*C*-CS<sub>3</sub>), 204.5 (NCS<sub>2</sub>), 233.4 (CS<sub>3</sub>). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\rm max}$  639, 483, 398 and 301.

The following complexes were synthesised using a one-pot procedure (b).

**Re(4-MePhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) (Re11).** Yield 56% (0.070 g). Elemental analysis: molecular formula C<sub>21</sub>H<sub>24</sub>NReS<sub>8</sub>·C<sub>2</sub>H<sub>5</sub>OH. Found: %C = 35.66, %H = 3.86, %S = 31.66; Calc. for [Re(4-MePhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>)]·C<sub>2</sub>H<sub>5</sub>OH: %C = 35.45, %H = 3.88, %S = 32.92. Mp = 178 °C. *R*<sub>f</sub> (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.43. IR (KBr disk) (cm<sup>-1</sup>): 1599 (w), 1506 (m), 1435 (w), 1353 (w), 1261 (s), 1209 (w), 1181 (w), 1096 (s), 1019 (s, *v*<sub>C-S</sub>), 912 (w), 867 (w), 802 (s), 703 (w), 662 (w), 544 (w, *v*<sub>S-S</sub>), 475 (w), 475 (w), 399 (m, *v*<sub>Re-S</sub>). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  1.10 (t, 3H, EtOH), 1.19 (t, *J* = 7.1 Hz, 6H, CH<sub>3</sub>), 2.62 (s, 6H, CH<sub>3</sub>), 3.40 (q, 2H, EtOH), 3.59 (m, 4H), 7.32 (dd, *J* = 8.6 Hz and *J* = 0.6 Hz, 4H, H<sub>aromatic</sub>), 7.97 (d, *J* = 8.2 Hz, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (100.67 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  13.2 (CH<sub>3</sub>), 21.5 (OCH<sub>3</sub>), 44.7 (CH<sub>2</sub>), 129.0 and 132.7 (CH<sub>aromatic</sub>), 133.0 (*C*-CH<sub>3</sub>), 144.1 (*C*-CS<sub>3</sub>), 206.9 (NCS<sub>2</sub>), 233.9 (CS<sub>3</sub>). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  639, 484, 400 and 326.

**Re(4-EtPhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) (Re12).** Yield 54% (0.070 g). Mp = 152 °C. *R*<sub>f</sub> (PE/CH<sub>2</sub>Cl<sub>2</sub>7/3) = 0.43. IR (KBr disk) (cm<sup>-1</sup>): 1601 (m), 1557 (m), 1506 (w), 1456 (m), 1412 (w), 1381 (w), 1353 (w), 1262 (s), 1209 (m), 1171 (m), 1096 (s), 1022 (s, *v*<sub>C-S</sub>), 929 (w), 882 (s), 802 (s), 764 (m), 702 (w), 646 (w), 616 (w), 555 (w, *v*<sub>S-S</sub>), 473 (w), 406 (m, *v*<sub>Re-S</sub>).<sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  1.19 (t, *J* = 7.1 Hz, 6H, CH<sub>3</sub>), 1.30 (t, *J* = 7.6 Hz, 6H, CH<sub>3</sub>), 2.87 (q, *J* = 7.8 Hz, 4H, CH<sub>2</sub>), 2.59 (qd, *J* = 7.1 Hz and *J* = 2.7 Hz, 4H, CH<sub>2</sub>), 7.35 (d, *J* = 8.3 Hz, 4H, H<sub>aromatic</sub>), 8.00 (d, *J* = 8.3 Hz, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (100.67 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  13.2 and 16.3 (CH<sub>3</sub>), 28.8 and 44.7 (CH<sub>2</sub>), 127.9 and 132.8 (CH<sub>aromatic</sub>), 133.1 and 150.3 (C<sub>aromatic</sub>), 204.9 (NCS<sub>2</sub>), 233.9 (CS<sub>3</sub>). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\rm max}$  639, 485, 402 and 323.

**Re(2-EtPhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) (Re13).** Yield 54% (0.048 g). Mp = 209 °C.  $R_f$  (PE/CH<sub>2</sub>Cl<sub>2</sub>7/3) = 0.48. IR (KBr disk) (cm<sup>-1</sup>): 1505 (s), 1478 (m), 1435 (s), 1354 (m), 1272 (s), 1209 (w), 1188 (w), 1148 (m), 1118 (w), 1077 (m), 1012 (s, v<sub>C-S</sub>), 944 (w), 913 (w), 852 (w), 785 (w), 752 (s), 648 (w), 578 (m, v<sub>S-S</sub>), 560 (w), 466 (w), 399 (m, v<sub>Re-S</sub>). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_H$  1.18 (t, *J* = 7.1 Hz, 6H, CH<sub>3</sub>), 1.25 (t, *J* = 7.5 Hz, 6H, CH<sub>3</sub>), 2.81 (q, *J* = 7.5 Hz, 4H, CH<sub>2</sub>), 3.50–3.66 (m, 4H, CH<sub>2</sub>), 7.29–7.40 (m, 4H, H<sub>aromatic</sub>), 7.43–7.50 (m, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (100.67 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_C$  13.1 (CH<sub>3</sub>), 16.6 (CH<sub>3</sub>), 26.9 (CH<sub>2</sub>), 44.8 (CH<sub>2</sub>), 125.9 129.7 130.9 and 132.8 (CH<sub>aromatic</sub>), 134.7 and 144.5 (C<sub>aromatic</sub>), 204.7 (NCS<sub>2</sub>), 235.6 (CS<sub>3</sub>). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  603, 464, 388 and 287.

Re(4-MeOPhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) (Re14). Yield 55% (0.072 g). Elemental analysis: molecular formula  $C_{21}H_{24}NO_2ReS_8$ .  $C_2H_5OH$ . Found: %C = 33.81, %H = 3.616, %S = 31.41; Calc. for [Re(4-MeOPhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>)]·C<sub>2</sub>H<sub>5</sub>OH: %C = 34.05, %H = 3.73, %S = 31.62. Mp = 181 °C.  $R_{f}$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.17. IR (KBr disk) (cm<sup>-1</sup>): 1594 (s), 1567 (w), 1504 (s), 1455 (m), 1434 (m), 1354 (w), 1300 (m), 1259 (s), 1173 (s), 1095 (m), 1025 (s, v<sub>C-s</sub>), 991 (w), 911 (w), 830 (m), 803 (m), 632 (w), 592 (m, v<sub>S-s</sub>), 545 (w), 480 (w), 399 (m, v<sub>Re-S</sub>).<sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  1.11 (t, 3H, EtOH), 1.19 (t, J = 7.0 Hz, 6H, CH<sub>3</sub>), 3.42 (q, 2H, EtOH), 3.60 (q, J = 7.3 Hz, 4H, CH<sub>2</sub>), 3.93 (s, 6H, OCH<sub>3</sub>), 7.01 (d, J = 9.0 Hz, 4H), 8.08 (d, J = 9.0 Hz, 4H). <sup>13</sup>C NMR (100.67 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  13.3 (CH<sub>3</sub>), 44.7 (CH<sub>2</sub>), 56.1 (OCH<sub>3</sub>), 113.8 and 128.9 (CH<sub>aromatic</sub>), 134.7 (C-CS<sub>3</sub>), 164.4 (C-OCH<sub>3</sub>), 205.1 (NCS<sub>2</sub>), 233.4 (CS<sub>3</sub>). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> 640, 487, 407 and 343.

**Re(3-MeOPhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) (Re15).** Yield 66% (0.086 g). Elemental analysis: molecular formula C<sub>21</sub>H<sub>24</sub>NO<sub>2</sub>ReS<sub>8</sub>.  $C_2H_5OH$ . Found: %C = 34.21, %H = 3.97, %S = 30.19; Calc. for  $[\text{Re}(3-\text{MeOPhCS}_3)_2(\text{Et}_2\text{NCS}_2)]\cdot\text{C}_2\text{H}_5\text{OH}: \%\text{C} = 34.05, \%\text{H} =$ 3.73, %S = 31.62. Mp = 92 °C.  $R_{\rm f}$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.13. IR (KBr disk) (cm<sup>-1</sup>): 1591 (m), 1573 (m), 1504 (m), 1456 (m), 1424 (m), 1377 (w), 1353 (w), 1319 (w), 1285 (m), 1261 (s), 1197 (w), 1161 (w), 1149 (w), 1095 (m), 1047 (s), 1019 (s, v<sub>C-s</sub>), 979 (w), 950 (w), 925 (w), 866 (w), 848 (w), 790 (w), 774 (m), 680 (s), 560 (m,  $v_{S-S}$ ).<sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{H}$  1.12 (t, 3H, EtOH), 1.20 (t, J = 7.1 Hz, 6H, CH<sub>3</sub>), 3.42 (q, 2H, EtOH), 3.60 (q, J = 7.0 Hz, 4H, CH<sub>2</sub>), 3.93 (s, 6H, OCH<sub>3</sub>), 6.87 (td, J = 8.2 Hz and J = 2.5 Hz, 2H, H<sub>aromatic</sub>), 7.43 (t, J = 8.2 Hz, 2H, H<sub>aromatic</sub>), 7.63 (m,4H, H<sub>aromatic</sub>).<sup>13</sup>C NMR (100.67 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  13.2 (CH<sub>3</sub>), 44.7 (CH<sub>2</sub>), 56.0 (OCH<sub>3</sub>), 117.5 119.4 125.7 129.3 (CH<sub>aromatic</sub>), 136.3 (C–CS<sub>3</sub>), 159.3 (C–OCH<sub>3</sub>), 205.6  $(NCS_2)$ , 233.6  $(CS_3)$ . UV/Vis  $(CH_2Cl_2)$ :  $\lambda_{max}$  640, 484, 401 and 300.

Re(2-MeOPhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) (Re16). Yield 37% (0.048 g). Elemental analysis: molecular formula C<sub>21</sub>H<sub>24</sub>NO<sub>2</sub>ReS<sub>8</sub>. Found: %C = 33.01, %H = 3.20, %S = 33.40; Calc. for [Re(2- $MeOPhCS_3_2(Et_2NCS_2)$ ]: %C = 32.96, %H = 3.16, %S = 33.52.  $Mp = 190 \degree C. R_f (PE/CH_2Cl_27/3) = 0.20. IR (KBr disk) (cm^{-1}):$ 1590 (w), 1505 (w), 1481 (w), 1456 (w), 1434 (w), 1261 (s), 1096 (s), 1077 (m), 1047 (m), 1019 (s, v<sub>C-s</sub>), 912 (w), 880 (w), 802 (s), 749 (m), 668 (w), 566 (w,  $v_{S-S}$ ), 460 (m), 409 (w,  $v_{Re-S}$ ). <sup>1</sup>H NMR  $(400.13 \text{ MHz}, \text{CDCl}_3, \text{SiMe}_4): \delta_{\text{H H}} 1.18 (t, J = 7.1 \text{ Hz}, 6\text{H}, \text{CH}_3),$  $3.59 (qd, J = 6.9 Hz, 4H, CH_2), 3.94 (s, 6H, OCH_3), 7.11 (d, J =$ 8.4 Hz, 2H,  $H_{aromatic}$ ), 7.16 (t, J = 7.4 Hz, 2H,  $H_{aromatic}$ ), 7.32 (m, 2H,  $H_{aromatic}$ ), 7.93 (dd, J = 7.8 Hz and J = 1.8 Hz, 2H,  $H_{aromatic}$ ). <sup>13</sup>C NMR (100.67 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  13.2 (CH<sub>3</sub>), 44.7 (CH<sub>2</sub>), 56.4 (OCH<sub>3</sub>), 111.1 120.8 125.8 and 133.5 (CH<sub>aromatic</sub>), 134.4 (C-CS<sub>3</sub>), 157.6 (C-OCH<sub>3</sub>), 205.5 (NCS<sub>2</sub>), 230.3 (CS<sub>3</sub>). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  629, 480, 395 and 293.

**Re(4-FPhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) (Re17).** Yield 12% (0.015 g). Mp = 163 °C.  $R_f$  (PE/CH<sub>2</sub>Cl<sub>2</sub>7/3) = 0.45. IR (KBr disk) (cm<sup>-1</sup>): 1592 (s), 1576 (w), 1558 (w), 1539 (w), 1499 (s), 1455 (w), 1435 (m), 1377 (w), 1353 (m), 1297 (w), 1264 (s), 1234 (s), 1211 (w), 1156 (s), 1098 (m), 1077 (m), 1045 (w), 1011 (s,  $v_{C-S}$ ), 954 (w), 913 (w), 888 (w), 829 (s), 805 (s), 632 (w), 587 (m), 542 (m), 428 (w,  $v_{Re-S}$ ). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_H$  1.20 (t, J = 7.1 Hz, 6H, CH<sub>3</sub>), 3.60 (qd, J = 7.1 Hz and J = 2.0 Hz, 4H, CH<sub>2</sub>), 7.22 (t, J = 8.4 Hz, 4H, H<sub>aromatic</sub>), 8.08 (dd, J = 8.6Hz and J = 5.3 Hz, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (100.67 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_C$  13.2 (CH<sub>3</sub>), 44.7 (CH<sub>2</sub>), 115.5 and 134.6 (CH<sub>aromatic</sub>), 131.6 (*C*-CS<sub>3</sub>), 166.7 (*C*-F), 204.6 (N*C*S<sub>2</sub>), 232.2 (CS<sub>3</sub>).

**Re(3-FPhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) (Re18).** Yield 38% (0.048 g). Mp = 207 °C.  $R_{\rm f}$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.47. IR (KBr disk) (cm<sup>-1</sup>): 1600 (m), 1579 (s), 1501 (s), 1484 (s), 1471 (s), 1432 (s), 1379 (w), 1358 (w), 1270 (s), 1258 (s), 1209 (m), 1148 (s), 1078 (w), 1011 (w), 1000 (m,  $v_{C-S}$ ), 985 (s,  $v_{C-S}$ ), 872 (s), 808 (s), 779 (s), 673 (m), 576 (w), 524 (w,  $v_{S-S}$ ), 458 (w), 405 (w,  $v_{Re-S}$ ). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{H}$  1.20 (t, J = 7.4 Hz, 6H, CH<sub>3</sub>), 3.60 (qd, J = 7.2 Hz and J = 3.0 Hz, 4H, CH<sub>2</sub>), 7.02 (td, J = 8.4 Hz and J = 2.6 Hz, 2H, H<sub>aromatic</sub>), 7.49 (qd, J = 5.7 Hz and J = 2.5 Hz, 2H, H<sub>aromatic</sub>), 7.49 (qd, J = 5.7 Hz and J = 2.5 Hz, 2Cl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{C}$  13.2 (CH<sub>3</sub>), 44.8 (CH<sub>2</sub>), 119.8 128.3 128.8 129.8 and 130.1 (CH<sub>aromatic</sub>), 136.6 (*C*-CS<sub>3</sub>), 162.1(C-F), 204.5 (NCS<sub>2</sub>), 231.4 (CS<sub>3</sub>). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  649, 486, 401 and 299.

#### Synthesis of technetium complexes

Bis-trithioperoxybenzoato dithiobenzoato complexes  $Tc(R-PhCS_3)_2(R-PhCS_2)$  were synthesised according to the procedure utilised for the unsubstituted  $Tc(PhCS_3)_2(PhCS_2)$  complex (**Tc1**).<sup>9</sup>

<sup>99</sup>**Tc(4-MePhCS<sub>3</sub>)<sub>2</sub>(4-MePhCS<sub>2</sub>) (Tc2).** Yield 92% (0.100 g).  $R_{\rm f}$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.79. IR (Nujol mull) (cm<sup>-1</sup>): 1600 (s), 1563 (m), 1544 (m), 1450 (s), 1377 (s), 1309 (w), 1279 (w), 1264 (m), 1205 (w), 1176 (s), 1018 (m,  $v_{\rm C-S}$ ), 948 (w), 889 (m), 815 (s), 768 (m), 758 (w), 637 (w), 620 (w), 549 (w,  $v_{\rm S-S}$ ), 503 (w), 464 (m,  $v_{\rm Tc-S}$ ). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  2.33 (s, 3H, CH<sub>3</sub>), 2.45 (s, 6H, CH<sub>3</sub>), 7.11 (d, J = 8.2 Hz, 2H, H<sub>aromatic</sub>), 7.25 (d, J = 8.0 Hz, 4H, H<sub>aromatic</sub>), 7.78 (d, J = 8.2 Hz, 2H, H<sub>aromatic</sub>), 7.97 (d, J = 8.1 Hz, 4H, H<sub>aromatic</sub>). NMR (75.48 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  22.0 (CH<sub>3</sub>), 124.9 129.3 129.8 and 136.1 (CH<sub>aromatic</sub>), 140.1 and 144.0 (C<sub>aromatic</sub>), 227.1 (CS<sub>3</sub>), 236.0 (CS<sub>2</sub>).

<sup>99</sup>**Tc(4-EtPhCS<sub>3</sub>)<sub>2</sub>(4-EtPhCS<sub>2</sub>) (Tc3).** Yield 92% (0.132 g).  $R_f$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.76. IR (Nujol mull) (cm<sup>-1</sup>): 1599 (s), 1461 (s), 1414 (w), 1376 (s), 1267 (s), 1232 (w), 1179 (s), 1130 (m), 1050 (w), 999 (s,  $v_{C-S}$ ), 964 (w), 950 (w), 910 (w), 832 (s), 769 (w), 669 (m), 593 (w), 569 (w), 553 (w,  $v_{S-S}$ ), 461 (m,  $v_{Tc-S}$ ), 440 (w). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_H$  1.19 (t, J = 7.6 Hz, 3H, CH<sub>3</sub>), 1.27 (t, J = 7.6 Hz, 6H, CH<sub>3</sub>), 2.63 (q, J = 7.9 Hz, 2H, CH<sub>2</sub>), 2.73 (q, J = 7.6, 4H, CH<sub>2</sub>), 7.14 (d, J = 8.6 Hz, 2H, H<sub>aromatic</sub>), 7.27 (d, J = 8.2 Hz, 4H, H<sub>aromatic</sub>), 7.80 (d, J = 8.4 Hz, 2H, H<sub>aromatic</sub>), 7.99 (d, J = 8.4 Hz, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_C$  15.7 and 15.8 (CH<sub>3</sub>), 29.3 and 29.4 (CH<sub>2</sub>), 125.0 128.1 128.7 and 129.9 (CH<sub>aromatic</sub>), 136.3 and 150.2 (C<sub>aromatic</sub>), 227.2 (CS<sub>3</sub>), 236.0 (CS<sub>2</sub>).

<sup>99</sup>**Tc(2-EtPhCS<sub>3</sub>)<sub>2</sub>(2-EtPhCS<sub>2</sub>) (Tc4).** Yield 59% (0.055 g).  $R_{\rm f}$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.70. IR (Nujol mull) (cm<sup>-1</sup>): 1459 (s), 1376 (s), 1258 (m), 1224 (w), 1188 (w), 1160 (w), 1120 (m), 1073 (m), 999 (s,  $v_{\rm C-S}$ ), 945 (m), 910 (w), 881 (w), 864 (w), 754 (s), 670 (m), 648 (m), 577 (w), 551 (w,  $v_{\rm S-S}$ ), 491 (w), 465 (m,  $v_{\rm Tc-S}$ ). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  1.18 (t, J = 5.8 Hz, 3H, CH<sub>3</sub>), 1.22 (t, J = 7.6 Hz, 6H, CH<sub>3</sub>), 2.71 (q, J = 7.5 Hz, 4H, CH<sub>2</sub>), 2.93 (q, J = 7.4 Hz, 2H, CH<sub>2</sub>), 7.16 (m, 2H, H<sub>aromatic</sub>), 7.31 (m, 3H, H<sub>aromatic</sub>), 7.41 (m, 7H, H<sub>aromatic</sub>). NMR (75.48 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  16.1 and 19.2 (CH<sub>3</sub>), 26.5 and 29.7 (CH<sub>2</sub>), 125.6 127.6 128.9 129.3 129.6 129.7 130.7 and 130.8 (CH<sub>aromatic</sub>), 131.0 136.6 140.8 and 142.1 (C<sub>aromatic</sub>), 229.1 (CS<sub>3</sub>), 242.6 (CS<sub>2</sub>).

<sup>99</sup>**Tc(4-MeOPhCS<sub>3</sub>)<sub>2</sub>(4-MeOPhCS<sub>2</sub>)** (**Tc5).** Yield 92% (0.140 g).  $R_f$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.25. IR (Nujol mull) (cm<sup>-1</sup>): 1595 (s), 1560 (w), 1542 (w), 1506 (m), 1469 (s), 1377 (s), 1305 (m), 1264 (s), 1237 (w), 1168 (s), 1074 (m), 1029 (s,  $v_{C-S}$ ), 949 (w), 829 (m), 739 (w), 668 (s), 594 (w,  $v_{S-S}$ ), 549 (w), 456 (m,  $v_{Tc-S}$ ). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_H$  3.82 (s, 3H, CH<sub>3</sub>), 3.89 (s, 6H, CH<sub>3</sub>), 6.80 (d, J = 7.7 Hz, 2H, H<sub>aromatic</sub>), 6.93 (d, J = 7.7 Hz, 4H, H<sub>aromatic</sub>), 7.87 (d, J = 8.5 Hz, 2H, H<sub>aromatic</sub>), 8.08 (d, J = 7.5 Hz, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_C$  56.1 (OCH<sub>3</sub>), 113.8 114.4 127.1 131.8 (CH<sub>aromatic</sub>), 132.1 (*C*-CS<sub>3</sub>), 137.0 (*C*-CS<sub>2</sub>), 163.9 and 164.4 (*C*-OCH<sub>3</sub>), 226.2 (CS<sub>3</sub>), 234.2 (CS<sub>2</sub>).

<sup>99</sup>Tc(3-MeOPhCS<sub>3</sub>)<sub>2</sub>(3-MeOPhCS<sub>2</sub>) (Tc6). Yield 59% (0.060 g).  $R_{\rm f}$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.19. IR (Nujol mull) (cm<sup>-1</sup>): 1596 (s), 1572 (s), 1488 (m), 1478 (m), 1427 (m), 1377 (m), 1323 (m), 1286 (s), 1263 (s), 1195 (w), 1163 (w), 1053 (m), 1020 (m), 1003 (m,  $v_{\rm C-S}$ ), 978 (m), 947 (w), 870 (s), 806 (w), 786 (s), 681 (s), 568 (m), 465 (m,  $v_{\rm Tc-S}$ ). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  3.80 (s, 3H, CH<sub>3</sub>), 3.90 (s, 6H, CH<sub>3</sub>), 7.01 (m, 3H, H<sub>aromatic</sub>), 7.24 (t, J = 8.0 Hz, 1H, H<sub>aromatic</sub>), 7.49 (dq, J = 7.6 and 0.7 Hz, 1H, H<sub>aromatic</sub>), 7.59–7.64 (m, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  30.2 and 56.1 (OCH<sub>3</sub>), 114.4 119.4 122.7 and 130.1 (CH<sub>aromatic</sub>), 141.5 and 159.9 (C<sub>aromatic</sub>), 227.1 (CS<sub>3</sub>), 236.1 (CS<sub>2</sub>).

<sup>99</sup>Tc(2-MeOPhCS<sub>3</sub>)<sub>2</sub>(2-MeOPhCS<sub>2</sub>) (Tc7). Yield 94% (0.066 g).  $R_{\rm f}$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.22. IR (Nujol mull) (cm<sup>-1</sup>): 1592 (m), 1569 (w), 1460 (s), 1376 (s), 1285 (m), 1246 (s), 1162 (m), 1110 (s), 1020 (s,  $v_{C-S}$ ), 975 (w), 944 (w), 785 (w), 753 (s), 668 (m), 649 (w), 571 (w,  $v_{s-s}$ ), 467 (s,  $v_{Tc-s}$ ).<sup>1</sup>H NMR  $(300.13 \text{ MHz}, \text{CDCl}_3, \text{SiMe}_4)$ :  $\delta_H$  3.84 (s, 3H, CH<sub>3</sub>), 3.92 (s, 6H, CH<sub>3</sub>), 6.89 (t, J = 7.8 Hz, 2H, H<sub>aromatic</sub>), 6.95 (t, J = 8.0 Hz, 2H, H<sub>aromatic</sub>), 7.03 (t, J = 7.8 Hz, 1H, H<sub>aromatic</sub>), 7.10 (t, J =7.3 Hz, 1H, H<sub>aromatic</sub>), 7.29 (t, J = 7.3 Hz, 2H, H<sub>aromatic</sub>), 7.43 (t, J = 7.4 Hz, 1H, H<sub>aromatic</sub>), 7.97 (dd, J = 7.7 and 1.5 Hz, 1H, H<sub>aromatic</sub>), 8.01 (dd, J = 5.3 and 1.8 Hz, 2H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  55.9 and 56.5 (OCH<sub>3</sub>), 111.9 112.6 120.4 121.4 129.4 and 131.4 (CHaromatic), 133.4 (C-CS<sub>3</sub>), 135.6 (C–CS<sub>2</sub>), 155.6 and 168.2 (C–OCH<sub>3</sub>), 222.3 (CS<sub>3</sub>), 232.5  $(CS_2).$ 

<sup>99</sup>**Tc(4-FPhCS<sub>3</sub>)<sub>2</sub>(4-FPhCS<sub>2</sub>) (Tc8).** Yield 86% (0.080 g).  $R_{\rm f}$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.67. IR (Nujol mull) (cm<sup>-1</sup>): 1592 (s), 1499 (s), 1458 (s), 1407 (w), 1376 (m), 1261 (m), 1239 (s), 1156 (s), 1003 (s,  $v_{\rm C-S}$ ), 948 (w,  $v_{\rm as C-S}$ ), 908 (s), 835 (s), 807 (w), 588 (m), 546 (m,  $v_{\rm S-S}$ ), 472 (m,  $v_{\rm Tc-S}$ ). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  7.02 (dd, J = 8.6 Hz, 2H, H<sub>aromatic</sub>), 7.16 (dd, J = 6.5 Hz, 4H, H<sub>aromatic</sub>), 7.88 (dd, J = 8.9 and 5.3 Hz, 2H, H<sub>aromatic</sub>), 8.09 (dd, J = 6.9 and 5.2 Hz, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  115.3 115.9 126.7 and 131.4 (CH<sub>aromatic</sub>), 134.3 and 138.8 (*C*-CS<sub>2</sub>), 165.6 and 166.2 (*C*-F), 225.3 (CS<sub>3</sub>), 234.2 (CS<sub>2</sub>).

<sup>99</sup>**Tc(3-FPhCS<sub>3</sub>)<sub>2</sub>(3-FPhCS<sub>2</sub>) (Tc9).** Yield 57% (0.035 g).  $R_{\rm f}$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.70. IR (Nujol mull) (cm<sup>-1</sup>): 1578 (s), 1559 (w), 1544 (m), 1508 (m), 1465 (s), 1376 (s), 1340 (w), 1284 (w), 1148 (w), 1097 (s), 984 (m,  $v_{C-S}$ ), 949 (m), 879 (s), 829 (m), 806 (m), 787 (m), 675 (s), 524 (w,  $v_{S-S}$ ), 471 (s,  $v_{Tc-S}$ ), 461 (s). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  7.11–7.22 (m, 3H, H<sub>aromatic</sub>), 7.32 (qd, J = 8.2 and 2.5 Hz, 1H, H<sub>aromatic</sub>), 7.44 (qd, J = 8.2 and 2.4 Hz, 2H, H<sub>aromatic</sub>), 7.55 (dt, J = 9.6 and 2.3 Hz, 1H, H<sub>aromatic</sub>), 7.65 (d, J = 8.3, 1H, H<sub>aromatic</sub>), 7.81 (m, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  111.6 116.7 119.7 and 125.7 (CH<sub>aromatic</sub>), 130.2 and 130.8 (*C*-CS<sub>2</sub>), 161.2 and 164.4 (*C*-F), 225.4, (CS<sub>3</sub>), 234.8 (CS<sub>2</sub>).

Bis-trithioperoxybenzoato diethyldithiocarbamato  $Tc(R-PhCS_3)_2(Et_2NCS_2)$  were prepared as detailed below.

To a CH<sub>2</sub>Cl<sub>2</sub> solution (5 mL) containing the relevant Tc(R-PhCS<sub>3</sub>)<sub>2</sub>(R-PhCS<sub>2</sub>) compound (0.050 mmol), diethyldithiocarbamate sodium salt (5 equivalents) dissolved in methanol (5 mL) was added dropwise and the solution stirred at room temperature for 2 h. The solvent was removed by evaporation under vacuum and the residue loaded onto a silica chromatography column and eluted with a mixture of petroleum ether and CH<sub>2</sub>Cl<sub>2</sub> (8 : 2, v/v). The pink band was collected, and, after removal of the solvent by evaporation under vacuum, a pink solid was obtained. Crystals suitable for X-ray diffraction studies were grown from a petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>/EtOH (1 : 1 : 1) mixture.

<sup>99</sup>**Tc(PhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) (Tc10).** Yield 66% (0.033 g).  $R_{\rm f}$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.50. IR (Nujol mull) 504 (s), 1499 (m), 1458 (m), 1440 (m), 1376 (w), 1274 (m), 1207 (m), 1180 (w),

1148 (m), 1074 (w), 1001 (m), 999 (s,  $\nu_{C-S}$ ), 904 (s), 756 (s), 731 (m), 683 (s). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  1.17 (t, J = 7.2 Hz, 6H, CH<sub>3</sub>), 3.66 (m, 4H, CH<sub>2</sub>), 7.46 (m, 6H, H<sub>aromatic</sub>), 8.10 (m, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  12.6 (CH<sub>3</sub>), 44.5 (CH<sub>2</sub>), 128.6 129.5 and 132.2 (CH<sub>aromatic</sub>), 138.2 (C<sub>aromatic</sub>), 200.0 (NCS<sub>2</sub>), 225.7 (CS<sub>3</sub>). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\rm max}$  525, 401 and 313.

<sup>99</sup>**Tc(4-MePhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) (Tc11).** Yield 55% (0.012 g).  $R_{\rm f}$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.43. IR (Nujol mull) (cm<sup>-1</sup>): 1597 (m), 1560 (w), 1509 (s), 1458 (s), 1376 (s), 1354 (w), 1277 (s), 1231 (w), 1210 (m), 1180 (s), 1148 (m), 1076 (w), 1016 (s,  $v_{\rm C-S}$ ), 949 (w), 907 (m), 812 (s), 735 (m), 669 (w), 637 (w), 585 (w), 546 (m,  $v_{\rm s-S}$ ), 483 (w), 444 (m,  $v_{\rm Tc-S}$ ).<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  1.17 (t, J = 7.2 Hz, 6H, CH<sub>3</sub>), 2.46 (s, 6H, CH<sub>3</sub>), 3.65 (q, J = 7.3 Hz, 4H, CH<sub>2</sub>), 7.26 (d, J = 4.0 Hz, 4H, H<sub>aromatic</sub>), 8.01 (d, J = 8.3 Hz, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm c}$  13.1 and 21.9 (CH<sub>3</sub>), 44.9 (CH<sub>2</sub>), 129.9 and 131.4 (CH<sub>aromatic</sub>), 143.3 and 148.2 (C<sub>aromatic</sub>), 195.9 (NCS<sub>2</sub>), 224.7 (CS<sub>3</sub>). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\rm max}$  526, 394 and 323.

<sup>99</sup>**Tc(4-EtPhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) (Tc12).** Yield 66% (0.025 g).  $R_{\rm f}$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.43. IR (Nujol mull) (cm<sup>-1</sup>): 1458 (s), 1376 (m), 1271 (m), 1179 (w), 1119 (s), 978 (m,  $v_{\rm C-S}$ ), 899 (s), 826 (w), 668 (m), 592 (w), 544 (w,  $v_{\rm S-S}$ ), 461 (m,  $v_{\rm Tc-S}$ ).<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  1.17 (t, J = 7.2 Hz, 6H, CH<sub>3</sub>), 1.28 (t, J = 7.6 Hz, 6H, CH<sub>3</sub>), 2.75 (q, J = 7.5 Hz, 4H, CH<sub>2</sub>), 3.65 (qd, J = 7.2 Hz and J = 2.7 Hz, 4H, CH<sub>2</sub>), 7.28 (d, J = 8.5 Hz, 4H, H<sub>aromatic</sub>), 8.03 (d, J = 8.3 Hz, 4H, H<sub>aromatic</sub>).<sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  13.1 and 15.9 (CH<sub>3</sub>), 29.2 and 44.9 (CH<sub>2</sub>), 128.5 and 130.0 (CH<sub>aromatic</sub>), 136.4 and 149.5 (C<sub>aromatic</sub>), 200.4 (NCS<sub>2</sub>), 226.2 (CS<sub>3</sub>). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\rm max}$  526, 398 and 324.

<sup>99</sup>**Tc(4-MeOPhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) (Tc14).** Yield 73% (0.028 g). *R*<sub>f</sub> (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.17. IR (Nujol mull) (cm<sup>-1</sup>): 1594 (m), 1559 (w), 1542 (w), 1506 (m), 1458 (s), 1418 (m), 1376 (s), 1302 (m), 1266 (s), 1200 (m), 1167 (s), 1118 (w), 1096 (s), 980 (m, *v*<sub>C-S</sub>), 944 (w), 917 (w), 831 (m), 789 (w), 739 (w), 668 (m), 592 (w, *v*<sub>S-S</sub>), 473 (m), 460 (m, *v*<sub>Tc-S</sub>). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>): *δ*<sub>H</sub> 1.17 (t, *J* = 7.4 Hz, 6H, CH<sub>3</sub>), 3.62–3.90 (m, 4H, CH<sub>2</sub>), 3.99 (s, 6H, CH<sub>3</sub>), 6.96 (dd, J = 8.4 Hz, 4H, H<sub>aromatic</sub>), 8.12 (d, J = 8.6 Hz, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>): *δ*<sub>C</sub> 13.0 (CH<sub>3</sub>), 44.8 (CH<sub>2</sub>), 56.1 (OCH<sub>3</sub>), 114.3 and 131.8 (CH<sub>aromatic</sub>), 129.3 (*C*-CS<sub>3</sub>), 163.6 (*C*-OCH<sub>3</sub>), 195.2 (NCS<sub>2</sub>), 225.4 (CS<sub>3</sub>). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): *λ*<sub>max</sub> 530, 413 and 351.

<sup>99</sup>Tc(3-MeOPhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) (Tc15). Yield 23% (0.006 g).  $R_{\rm f}$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.13. IR (Nujol mull) (cm<sup>-1</sup>): 1593 (w), 1576 (w), 1489 (m), 1458 (s), 1376 (s), 1285 (s), 1269 (s), 1120 (s), 1075 (s), 1020 (m), 967 (s,  $v_{\rm C-S}$ ), 911 (m), 787 (m), 741 (w), 668 (w), 542 (m), 470 (s,  $v_{\rm Te-S}$ ). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  1.17 (t, J = 7.2 Hz, 6H, CH<sub>3</sub>), 3.66 (m, 4H, CH<sub>2</sub>), 3.92 (s, 6H, CH<sub>3</sub>), 7.00 (m, 2H, H<sub>aromatic</sub>), 7.36 (m, 2H, H<sub>aromatic</sub>), 7.51– 7.55 (m, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  13.1 (CH<sub>3</sub>), 44.9 (CH<sub>2</sub>), 56.1 (OCH<sub>3</sub>), 114.7 118.7 122.8 and 129.9 (CH<sub>aromatic</sub>), 139.6 and 159.9 (C<sub>aromatic</sub>), 200.4 (NCS<sub>2</sub>), 225.9 (CS<sub>3</sub>). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\rm max}$  526 and 385.

<sup>99</sup>**Tc(4-FPhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) (Tc17).** Yield 89% (0.025 g).  $R_{\rm f}$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.45. IR (Nujol mull) (cm<sup>-1</sup>): 1592 (s), 1560 (w), 1499 (s), 1458 (s), 1406 (w), 1376 (s), 1297 (w), 1273 (m), 1237 (s), 1157 (s), 1077 (w), 1011 (m,  $v_{\rm C-S}$ ), 913 (w), 830 (s), 806 (m), 608 (w), 588 (m), 544 (m,  $v_{\rm S-S}$ ), 472 (m,  $v_{\rm Te-S}$ ). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  1.18 (t, J = 7.1 Hz, 6H, CH<sub>3</sub>), 3.66 (m, 4H, CH<sub>2</sub>), 7.16 (dd, J = 8.5 Hz, 4H, H<sub>aromatic</sub>), 8.12 (dd, J = 8.6 and 5.3 Hz, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  13.1 (CH<sub>3</sub>), 44.9 (CH<sub>2</sub>), 116.2 and 131.84 (CH<sub>aromatic</sub>), 129.1 (*C*-CS<sub>3</sub>), 165.9 (*C*-F), 200.3 (NCS<sub>2</sub>), 224.5 (CS<sub>3</sub>). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\rm max}$  526, 403 and 312.

<sup>99</sup>**Tc(3-FPhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) (Tc18).** Yield 50% (0.006 g).  $R_{\rm f}$  (PE/CH<sub>2</sub>Cl<sub>2</sub> 7/3) = 0.47. IR (Nujol mull) (cm<sup>-1</sup>): 1579 (m),

1559 (w), 1542 (w), 1522 (w), 1498 (m), 1458 (s), 1436 (w), 1376 (m), 1266 (m), 1209 (w), 1146 (w), 1099 (s), 985 (m,  $v_{C-S}$ ), 948 (w), 916 (w), 869 (w), 808 (w), 769 (m), 679 (m), 669 (m), 471 (m,  $v_{Tc-S}$ ). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm H}$  1.18 (t, J = 7.2 Hz, 6H, CH<sub>3</sub>), 3.65 (m, 4H, CH<sub>2</sub>), 7.16 (t, J = 8.2 Hz, 2H, H<sub>aromatic</sub>), 7.44 (q, J = 8.2 Hz, 2H, H<sub>aromatic</sub>), 7.86 (t, J = 7.1 Hz, 4H, H<sub>aromatic</sub>). <sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>):  $\delta_{\rm C}$  13.1 (CH<sub>3</sub>), 45.0 (CH<sub>2</sub>), 116.7 119.1 125.9 and 130.5 (CH<sub>aromatic</sub>), 140.0 (*C*-CS<sub>2</sub>), 164.4 (*C*-F), 200.2 (N*C*S<sub>2</sub>), 223.9 (CS<sub>3</sub>). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\rm max}$  529, 403, and 312.

#### Determination of the structures

The X-ray data collections of Re2, Re10 and Tc10 EtOH were performed at room temperature with a Nicolet R3m/V fourcircle diffractometer on single crystals mounted in a thin walled glass capillary, with graphite monochromated Mo-Ka radiation  $(\lambda = 0.71073 \text{ Å})$ . The positions of the heavier atoms were determined by Patterson function and subsequent Fourierdifference syntheses revealed the positions of the other nonhydrogen atoms. Solution of the structures was performed with SHELXTL NT<sup>18</sup> and refined by full-matrix least-squares methods on  $F^2$ . After some cycles of refinement, performed with the SHELXL-97 program,<sup>19</sup> in Tc10 an EtOH molecule afflicted with high thermal motion appeared, and its atoms were refined isotropically. In Re10 the carbon atoms C(6) and C(7) of an ethyl group were each disordered over two positions. The site occupancy factors of the disordered atoms were refined and the multiplicity resulted ca. 2/3: 1/3. All non-H atoms were refined anisotropically, while H atoms were placed geometrically and allowed to ride on their attached atoms with isotropic thermal parameters according to the atoms to which they were attached. As a common feature, in all determinations the methyl H atoms were not apparent from the difference map and they were not included in the refinement procedure. In the final difference maps some peaks (up to 1.9 e Å<sup>-3</sup>, 0.88 Å from Re in Re10) were considered to be noise. Crystal data, summary of data collection and structure refinement are collected in Table 1.

CCDC reference numbers 264127-264129.

See http://dx.doi.org/10.1039/b503938j for crystallographic data in CIF or other electronic format.

## **Results and discussion**

## Synthesis

As sketched in Scheme 1, reduction–substitution reactions of labile  $[MOCl_4]^-$  precursors with an excess of dithiobenzoate  $(PhCS_2)^-$  or substituted dithiobenzoates  $(R\text{-}PhCS_2)^-$  ligands in

dichloromethane/methanol solutions gave mixed neutral bistrithioperoxy/dithiobenzoato M<sup>III</sup>(R-PhCS<sub>3</sub>)<sub>2</sub>(R-PhCS<sub>2</sub>) complexes M1-9 in moderate (for Re) to high (for Tc) yields. As described previously, the reaction took place through reduction of the metal centre and oxidation of the dithiobenzoate ligand to trithiobenzoate.8,9 The insertion of electron-donating substituents at the dithiobenzoate fragment did not significantly modify the reaction profile nor the recovered yields. The unique dithiobenzoate ligand was found to be labile, irrespective of the substituent incorporated on the phenyl ring. Hence, reactions of these  $M(R-PhCS_3)_2(R-PhCS_2)$  complexes with an excess of diethyldithiocarbamate (Et<sub>2</sub>NCS<sub>2</sub>)<sup>-</sup> afforded another class of mixed neutral bis-trithioperoxybenzoato dithiocarbamato M(R-PhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) compounds M10-18. In the case of rhenium, formation of mixed ligand Re(R-PhCS<sub>3</sub>)<sub>2</sub>-(Et<sub>2</sub>NCS<sub>2</sub>) compounds also could be achieved using a direct procedure by mixing [ReOCl<sub>4</sub>]<sup>-</sup> with an excess of both dithiobenzoate and dithiocarbamate ligands in methanol. In the case of technetium, such a simplified reaction pathway does not work, and mixtures of unsubstituted and dithiocarbamate-substituted compounds were collected along with several uncharacterised impurities.

Thin layer chromatography performed on silica gel plates indicated that: i) isostructural technetium and rhenium compounds showed identical  $R_f$  values (see Experimental section), ii) compounds bearing alkyl substituted and fluoro-substituted phenyl groups are the most lipophilic of the series with  $R_f$ values in the 0.67–0.79 range, while methoxy substituents gave rise to less lipophilic species ( $R_f$  in the 0.19–0.25 range), iii) dithiocarbamate containing **M10–18** compounds displayed less lipophilic character than the corresponding dithiobenzoate containing **M1–9** compounds.

#### Characterization

Elemental analysis of rhenium compounds, as shown in the Experimental section, are in good agreement with the proposed formulation. The IR spectra of all of the complexes show no retention of the monooxo-metal stretching vibration, but exhibit absorptions typical of coordinated trithio- and dithio-benzoate or dithiocarbamate ligands at *ca.* 1590, 1000, 550 and 400 cm<sup>-1</sup>.

NMR spectra show profiles characteristic of diamagnetic species, which are in agreement with the low spin d<sup>4</sup> electron configuration typical of trigonal prismatic M(III) compounds (*vide infra*). In detail, <sup>1</sup>H NMR spectra of  $M(R-PhCS_3)_2(R-PhCS_2)$  show two set of  $A_2B_2$  (phenyl *para*-substituted derivatives **M2**, **M3**, **M5** and **M8**), or ABCE (phenyl *meta*-substituted **M6** and **M9**) or ABCD (phenyl *ortho*-substituted **M4** and **M7**)

Table 1 Crystal data and details of data collection for Re2, Re10 and Tc10 EtOH

	Re2	Re10	Tc10-EtOH
Empirical formula	$C_{24}H_{21}ReS_8$	$C_{19}H_{20}NReS_8$	C <sub>21</sub> H <sub>26</sub> NOTcS <sub>8</sub>
M	752.09	705.04	662.91
Crystal system; space group	Triclinic; P1 (No. 2)	Orthorhombic; Pca2 <sub>1</sub> (No. 29)	Triclinic; P1 (No. 2)
a/Å	5.984(1)	12.503(3)	9.913(2)
b/Å	12.106(2)	10.546(2)	10.414(2)
c/Å	20.618(4)	19.355(4)	14.912(3)
a/°	101.61(3)	90	109.94(3)
8/°	92.87(3)	90	90.39(3)
γ/°	94.22(3)	90	108.16(3)
$V/Å^3$	1455.9(5)	2552.1(9)	1364.0(5)
$Z, D_{\text{calcd}}/\text{Mg m}^{-3}$	2; 1.716	4; 1.835	2; 1.614
$\lambda/\text{\AA}; \mu/\text{cm}^{-1}$ Refins collected	0.71073; 47.6	0.71073; 54.2	0.71073; 11.6
	5083	2343	5035
Refins obsd $(I > 2\sigma(I))$	2702	2039	4918
R1 <sup>a</sup> (obsd reflns)	0.048	0.055	0.052
$wR2^{b}$ (obsd reflns)	0.091	0.142	0.135
$\operatorname{GOF}^c$ on $F^2$	0.810	1.013	1.191
Largest peak/e Å <sup>-3</sup>	1.07 (1.15 Å far from Re)	1.88 (0.90 Å far from Re)	0.92 (0.98 Å far from Tc)

 ${}^{a}R1 = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|. {}^{b}wR2 = [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2}/\Sigma w(F_{o}^{2})^{2}]^{1/2}. {}^{c}GOF = [\Sigma w(|F_{o}^{2}| - |F_{c}^{2}|)^{2}]/(N_{obsd} - N_{params})]^{1/2}.$ 

### M(R-PhCS<sub>3</sub>)<sub>2</sub>(R-PhCS<sub>2</sub>)



Scheme 1

aryl protons (relative integration 2 : 1), and two set of aliphatic protons (relative integration 2 : 1) for alkyl substituted phenyl ligands (**M2–7** species), indicating the existence of different coordinating trithioperoxybenzoate and dithiobenzoate phenyl rings. This feature is confirmed by the occurrence of two dithiocarboxy signals in the 222–244 ppm region in the corresponding <sup>13</sup>C spectra. On the other hand, M(R-PhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) complexes, **M10–18**, exhibit a unique set of aryl protons (those arising from the two magnetically equivalent trithioperoxybenzoate phenyl rings) along with the signals of the dithiocarbamate residue. According to the different nature of the trithioperoxybenzoate and dithiocarbamate fragments two dithiocarboxy signals are still observed in the <sup>13</sup>C spectra in the 196–235 ppm region. The dithiocarbamate carboxy signal falls consistently around 205 ppm in the rhenium complexes, while it is more shielded (196–200 ppm) in the technetium analogs.

The cyclic voltammetric data of selected Re and Tc compounds are reported in Table 2. As depicted in the voltammogram shown in Fig. 1, two-reversible one-electron oxidations and one reversible cathodic wave are observed for the representative  $Tc(PhCS_3)_2(Et_2NCS_2)$  (**Tc10**) compound.

The oxidations are assigned by coulombmetric experiments to the formation of Tc(IV) and Tc(V), respectively, presumably accessing the 5d<sup>3</sup> and 5d<sup>2</sup> systems, whereas the reduction is assigned to the Tc(III)/Tc(II) couple. As expected on the basis of previous investigations on isostructural technetium and

Table 2 Cyclic voltammetric data for some Re(III) and Tc(III) complexes recorded at 200 mV s<sup>-1</sup>, referenced to the Fc/Fc<sup>+</sup> couple

Compound		M = Re	Redox couple	M = Tc
$M(PhCS_3)_2(PhCS_2)$	M1	+0.580	M(III)/M(IV)	+0.894
		-1.090	M(IV)/M(V)	$+1.362^{a}$
			M(III)/M(II)	-0.556
M(4-MeOPhCS <sub>3</sub> ) <sub>2</sub> (4-MeOPhCS <sub>2</sub> )	M5	+0.225	M(III)/M(IV)	+0.300
		+0.587	M(IV)/M(V)	+0.775
		$-1.320^{a}$	M(III)/M(II)	-1.056
$M(3-MeOPhCS_3)_2(3-MeOPhCS_2)$	M6	с	M(III)/M(IV)	+0.450
		с	M(IV)/M(V)	$+0.950^{a}$
			M(III)/M(II)	-0.944
$M(4-FPhCS_3)_2(4-FPhCS_2)$	M8	+0.275	M(III)/M(IV)	+0.480
		$+0.637^{b}$	M(IV)/M(V)	$+0.955^{a}$
		$-1.412^{a}$	M(III)/M(II)	-0.945
$M(PhCS_3)_2(Et_2NCS_2)$	M10	+0.050	M(III)/M(IV)	+0.194
		+0.362	M(IV)/M(V)	+0.756
		$-1.412^{a}$	M(III)/M(II)	-1.125
$M(4-MeOPhCS_3)_2(Et_2NCS_2)$	M14	-0.005	M(III)/M(IV)	с
		+0.455	M(IV)/M(V)	с
		$-1.468^{a}$	M(III)/M(II)	
$M(3-MeOPhCS_3)_2(Et_2NCS_2)$	M15	+0.110	M(III)/M(IV)	с
		+0.530	M(IV)/M(V)	c
		$-1.370^{a}$	M(III)/M(II)	

<sup>*a*</sup> Irreversible process (by changing the potential scan speed from 50 to 400 mV s<sup>-1</sup> the corresponding anodic wave is never observed). <sup>*b*</sup> Anodic process followed by chemical reaction. <sup>*c*</sup> Adsorption process on the electrode surface.



**Fig. 1** Cyclic voltammogram of  ${}^{99}$ Tc(PhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) (**Tc10**) in the -1.5 to +1.5 V region, 0.2 V cm<sup>-1</sup>, Ag wire quasi-reference electrode:  $3.5 \times 10^{-3}$  M complex, 0.1 M [Bu<sub>4</sub>N][ClO<sub>4</sub>] in dry and degassed CH<sub>2</sub>Cl<sub>2</sub>.

rhenium systems,<sup>2</sup> rhenium complexes are generally easier to oxidise and more difficult to reduce than the corresponding technetium species. In addition, for rhenium complexes, the reduction process is irreversible. The insertion of electron donor substituents on the dithiobenzoate phenyl framework, which increases the electron density at the metal centre, makes the resulting  $M(R-PhCS_3)_2(R-PhCS_2)$  complexes easier to oxidise by 300-600 mV and more difficult to reduce by 230-500 mV than the corresponding unsubstituted phenyl derivatives M1. Analogously, the substitution of the diethyldithiocarbamate for the dithiobenzoate fragment in M(PhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) derivatives (M10) produces easier oxidation and more difficult reduction processes compared to the dithiobenzoato analogues M1. Such effects are magnified in the technetium compounds. For example, in Tc10 the Tc(III)/Tc(IV) and Tc(III)/Tc(II) processes occur at more negative values by 700 and 570 mV, respectively, compared to those observed in Tc1, while the corresponding Re(III)/Re(IV) and Re(III)/Re(II) processes occur at more negative values by 530 and 320 mV for Re10 compared to Re1.

Red-ox potentials exhibited by the M(III)/M(II)and M(III)/M(IV) couples in **M10** compounds resemble those reported for analogous 'sulfur rich' mixed-ligand complexes  $[M(9S3)(SSS)]^+$  (M = Tc, Re; 9S3 = 1,4,7-trithiacyclononane; SSS = SCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>S).<sup>20</sup> For example, in the rhenium complex [Re(9S3)(SSS)]<sup>+</sup> oxidation to Re(IV) is reported to occur at +0.015 V and reduction to Re(II) at -1.350 V, values to be compared with +0.050 and -1.412 V detected for the corresponding couples in **Re10**.

Electronic spectra of both dithiobenzoate containing M(R-PhCS<sub>3</sub>)<sub>2</sub>(R-PhCS<sub>2</sub>) M1-9 and dithiocarbamate containing M(R-PhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>) M10-18 compounds are dominated by three different absorption bands: those occurring beyond 550 nm ( $\varepsilon$  ca. 1000 M<sup>-1</sup> cm<sup>-1</sup>) are attributed to d–d spectral transitions and are responsible for the green colour of the rhenium compounds. Pink-violet technetium complexes show red-shifted shoulders at 650-660 nm (Fig. 2, top spectra). Absorptions in the 480–400 nm (for Re) and 530–400 nm (for Tc) ranges ( $\varepsilon$  ca.  $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) are assigned to charge transfer transitions. The latter corresponds to ligand (sulfur) to metal charge transfer (LMCT) bands. High energy absorptions ( $\varepsilon > 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) in the UV region are attributed to internal  $\pi$ - $\pi$ \* HOMO/LUMO ligand transitions. A red shift of higher wavelength (lower energy) bands is observed on going from dithiobenzoate containing M(R-PhCS<sub>3</sub>)<sub>2</sub>(R-PhCS<sub>2</sub>) to dithiocarbamate containing  $M(R-PhCS_3)_2(Et_2NCS_2)$  complexes, as it appears from the comparison of the electronic spectra of [Re(4-MeOPhCS<sub>3</sub>)<sub>2</sub>(4-MeOPhCS<sub>2</sub>)] Re5 and [Re(4-MeOPhCS<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>NCS<sub>2</sub>)] Re14 re-





Fig. 2 Electronic spectra of  $Re(4-MePhCS_3)_2(4-MePhCS_2)$  (Re2; black line) and <sup>99</sup>Tc(4MePhCS\_3)\_2(4-MePhCS\_2) (Tc2; gray line) (top spectra); comparison of electronic spectra of  $Re(4-OMePhCS_3)_2$ -(4-OMePhCS\_2) (Re5; black line) and  $Re(4-MePhCS_3)_2$ (Et<sub>2</sub>NCS<sub>2</sub>) (Re14; gray line) (bottom spectra).

ported in Fig. 2, bottom spectra. This behaviour is in agreement with the greater electron-donating character of dithiocarbamate compared to dithiobenzoate ligands.

## X-Ray crystal structure analysis

The ORTEP<sup>21</sup> drawings of the complexes **Re2** and **M10** EtOH, together with the numbering scheme used, are shown in Figs. 3 and 4 (ORTEP of **Re10**, isostructural with **Tc10**, is not shown); relevant bond lengths and angles are reported in Table 3. The 'inner core' of the three complexes adopts a distorted trigonal

 Table 3
 Selected bond distances (Å) and angles (°) for Re2, Re10 and Tc10 EtOH

	Re2	Re10	Tc10·EtOH
M-S(1)	2.352(3)	2.385(5)	2.344(1)
M-S(2)	2.221(3)	2.237(5)	2.221(2)
M-S(4)	2.354(3)	2.365(5)	2.346(1)
M-S(5)	2.226(3)	2.240(5)	2.233(1)
M-S(7)	2.495(4)	2.527(5)	2.508(2)
M-S(8)	2.501(4)	2.513(5)	2.497(2)
S(2)–S(3)	2.100(4)	2.140(7)	2.096(2)
S(5)–S(6)	2.116(5)	2.126(7)	2.097(2)
S(1)-M-S(2)	88.8(1)	89.0(2)	89.45(5)
S(4) - M - S(5)	89.4(1)	89.9(2)	89.69(5)
S(7)-M-S(8)	67.6(1)	68.5(2)	69.04(6)
M-S(1)-C(1)	112.7(4)	111.4(7)	111.8(2)
M-S(2)-S(3)	111.3(2)	110.7(3)	110.64(7)
M-S(4)-C(2)	110.9(4)	112.6(8)	111.9(2)
M-S(5)-S(6)	110.1(2)	110.3(3)	110.11(7)
M-S(7)-C(3)	90.5(5)	90.5(8)	89.3(2)
M-S(8)-C(3)	91.3(5)	89.8(7)	89.5(2)
S(2)-S(3)-C(1)	105.3(4)	104.3(7)	104.9(2)
S(5)-S(6)-C(2)	104.1(4)	104.7(7)	105.2(2)
S(1)-C(1)-S(3)	121.8(7)	122.5(9)	122.8(3)
S(4)-C(2)-S(6)	125.0(7)	122.3(9)	123.0(3)
S(7)–C(3)–S(8)	110.5(9)	111(1)	112.2(3)

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Fig. 3 The ORTEP diagram of **Re2** showing essential numbering. Hydrogen atoms are omitted for clarity; ellipsoids are drawn at the 40% probability level.



Fig. 4 The ORTEP diagram of Tc10 EtOH showing essential numbering. Hydrogen atoms and EtOH molecule are omitted for clarity; ellipsoids are drawn at the 40% probability level. (Compound Re10 is isostructural with Tc10.)

prism environment realized by six sulfur atoms, with metal–S distances encompassing a wide range, from 2.221(3) to 2.527(5) Å. In the three complexes the two trithioperoxybenzoate and the third chelating ligands define, respectively, two five-membered

and one four-membered ring around the metal centre. The four-membered rings of the three complexes are planar and the same can be said of the five-membered rings defined by the M, S(4), S(5), S(6), C(2) atoms. The remaining five-membered ring of **Re10** and **Tc10**-EtOH assumes instead a somewhat *envelope* conformation with the metal atom 'at the flap' (by 0.39 and 0.13 Å, respectively), while planarity is confirmed for **Re2**.

Comparison of M–S bond lengths of isostructural mononuclear Re(III) and Tc(III) complexes collected in this work with the structural data of **M1** compounds reported previously<sup>8,9</sup> reveals that in all cases the coordination sphere comprises several types of metal–sulfur interactions (Table 4). Shorter distances include covalent metal–thiolate bonds (2.20–2.24 Å) and coordinative metal–sulfur bonds (2.32–2.38 Å) of the trithioperoxybenzoate moieties. Longer distances belong to the unique dithiobenzoate (or dithiocarbamate) ligand (2.45–2.53 Å).

In unsubstituted phenyl complexes  $M(PhCS_3)_2(PhCS_2)$  (M1), the Tc–S distances are roughly 0.03 Å longer than the corresponding Re–S distances, whereas the reverse situation is found in dithiocarbamate containing complexes  $M(PhCS_3)_2(Et_2NCS_2)$ (M10), which show slightly shorter Tc–S distances compared to Re–S ones. In the series of three rhenium complexes, a lengthening of the Re–S bonds is observed by increasing the electron donating character of the ligand donor set on going from **Re1** to **Re2** and to **Re10**. This behaviour indicates that the metal, while accepting more negative charge from the ligand set, needs to redistribute this excess electron density over a larger volume, and to transfer electrons more readily in the oxidation processes. In fact, **Re10** undergoes oxidation to Re(IV) at less positive values (+ 0.050 V) than **Re2** (+ 0.225 V) and **Re1** (+ 0.580 V).

The peculiar stoichiometry of  $M(R-PhCS_3)_2(R-PhCS_2)$ and  $M(R-PhCS_3)_2(Et_2NCS_2)$  deserves an additional comment. While oxidation of dithiobenzoate to trithioperoxybenzoate is required to balance the reduction of rhenium,<sup>22</sup> the use of a further excess of dithiobenzoate in the reduction–substitution reactions starting from  $[MO_4]^-$  does not modify the 2 : 1 trithioperoxybenzoate : dithiobenzoate ratio,<sup>11</sup> although oxidation of a third dithiobenzoate would be accessible from a stoichiometric point of view. The stability of the  $[M^{III}(R-PhCS_3)_2]^+$  moiety, which is further confirmed by the one-pot

**Table 4** Comparison of some bond lengths (Å) and angles (°) reported for five homologous  $[M^{III}(SS)_3]$  neutral complexes (M = Tc, Re; SS = bidentate ligand with sulfur donor atom)



	Tc1	Tc10·EtOH	Re1	Re2	Re10
Reference	9	This work	8	This work	This work
M-S(1)	2.349(4)	2.344(1)	2.318(2)	2.352(3)	2.385(5)
M-S(2)	2.231(4)	2.221(2)	2.197(2)	2.221(3)	2.237(5)
M-S(4)	2.354(4)	2.346(1)	2.321(2)	2.354(3)	2.365(5)
M-S(5)	2.227(4)	2.233(1)	2.200(2)	2.226(3)	2.240(5)
M-S(7)	2.510(4)	2.508(2)	2.481(2)	2.495(4)	2.527(5)
M-S(8)	2.478(5)	2.497(2)	2.449(2)	2.501(4)	2.513(5)
S(2) - S(3)	2.099(6)	2.096(2)	2.103(3)	2.100(4)	2.140(7)
S(5)–S(6)	2.075(6)	2.097(2)	2.068(3)	2.116(5)	2.126(7)
S(1)-M-S(2)	89.6(1)	89.45(5)	89.1(1)	88.8(1)	89.0(2)
S(4) - M - S(5)	89.2(1)	89.69(5)	88.9(1)	89.4(1)	89.9(2)
S(7) - M - S(8)	68.1(1)	69.04(6)	67.7(1)	67.6(1)	68.5(2)
S(1) - M - S(4)	175.4(1)	177.60(5)	175.6(1)	176.8(1)	176.9(2)
$\varepsilon^{a}$	17.1	9.8	8.9	11.8	8.4

<sup>a</sup> Twist angle between the upper S(1)S(5)S(7) and the lower S(2)S(4)S(8) triangular faces.

formation of the mixed compounds containing a dithiocarbamate ligand, arises from the appropriate matching of M(III) electronic requirements with  $\pi$ -donor (covalent thiolate S) and  $\pi$ -acceptor (coordinative thiourea S) properties of the trithioperoxybenzoate groups. The arrangement of this metalfragment partially mimics the trigonal bipyramidal (tbp) geometry typical of M(III) complexes. However, in the presence of dithiobenzoate or dithiocarbamate, able to delocalize electron density *via*  $\pi$ -orbitals, [M(R-PhCS<sub>3</sub>)<sub>2</sub>]<sup>+</sup> does not evolve to a five-coordinate tbp, but to the less common six-coordinate trigonal prismatic array. The expansion of the coordination number is balanced by the lengthening of the bonds of the 'third' bidentate ligand (dithiobenzoate or dithiocarbamate).

# Conclusions

Two series of neutral, lipophilic Tc(III) and Re(III) mixed-ligand complexes comprising trithioperoxybenzoate and dithiobenzoate (or dithiocarbamate) have been prepared and fully characterised. The coordination sphere of the metal is completely filled by six sulfur donor atoms arising from two bidentate trithioperoxybenzoate and a bidentate dithiobenzoate (or dithiocarbamate) ligand arranged in a distorted trigonal prismatic geometry.

In mixed trithioperoxybenzoate/dithiobenzoate complexes **M2–9** the insertion of variable substituents on the phenyl ring does not alter the stoichiometry, stereochemistry and stability of the resulting compounds, but modifies their overall lipophilicity and red-ox properties. These variations might be profitably utilised to tune the biological properties of this class of compounds when prepared at nanomolar level with <sup>99m</sup>Tc and <sup>188</sup>Re.

While the bis-trithioperoxybenzoato metal moiety is substitution-inert because of the appropriate balance of donor/ acceptor properties provided by the different sulfur atoms in the bis-bidentate chelator, the unique dithiobenzoate is labile and can be efficiently exchanged with better nucleophiles such as dithiocarbamates, producing a series of more stable mixed trithioperoxybenzoate/dithiocarbamate complexes **M10–18**. If the M–dithiocarbamate bond proves to be kinetically stable in biological media, the availability of this ligand-exchange route offers the possibility of introducing biologically active molecules appended to the dithiocarbamate fragment.

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