

Rhenium Complexes Containing an η^2 -Thiocarbamoyl Group: Synthesis, Electrochemistry, and Crystal Structure of $[\text{Re}(\text{S}_2\text{CNEt}_2)_2(\text{SCNEt}_2)(\text{PPh}_3)]\text{ClO}_4$

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A new redox couple of rhenium complexes, $[\text{Re}^{\text{III}}(\text{S}_2\text{CNEt}_2)_2(\text{SCNEt}_2)(\text{PPh}_3)]$ and $[\text{Re}^{\text{IV}}(\text{S}_2\text{CNEt}_2)_2(\text{SCNEt}_2)(\text{PPh}_3)]\text{ClO}_4$, has been isolated and electrochemically characterized; the η^2 -co-ordination of the *N,N*-diethylthiocarbamoyl group in the latter has been confirmed by X-ray analysis.

The *N,N*-dialkylthiocarbamoyl ligand (SCNR_2), having carbene character, co-ordinates to metals in three different modes; $\sigma^1\text{-C}$, $\eta^2\text{-C,S}$, and $\mu\text{-C,S}$.¹ Thiocarbamoyl complexes have most often been synthesized by oxidative addition of R_2NCSX .^{1,2} There are several reports, however, of conversion of a dithiocarbamate ligand into a thiocarbamoyl ligand.³ We report the first thiocarbamoyl rhenium complexes, synthesized directly by the latter method.

The reaction of *trans*- $[\text{ReCl}_3(\text{CH}_3\text{CN})(\text{PPh}_3)_2]$ with a large

excess of $\text{NaS}_2\text{CNEt}_2$ in acetone[†] produces $[\text{Re}^{\text{III}}(\text{S}_2\text{CNEt}_2)_2(\text{SCNEt}_2)(\text{PPh}_3)]$ (**1**), which is readily oxidized by $\text{K}_3[\text{Fe}(\text{CN})_6]$ to the cationic complex $[\text{Re}^{\text{IV}}(\text{S}_2\text{CNEt}_2)_2\text{-}$

[†] Following the methods of Rowbottom and Wilkinson,⁴ we were attempting to obtain $\text{Re}(\text{S}_2\text{CNEt}_2)_3$. In the event the main product was the complex (**1**) and $\text{Re}(\text{S}_2\text{CNEt}_2)_3$ was only a minor contaminant.

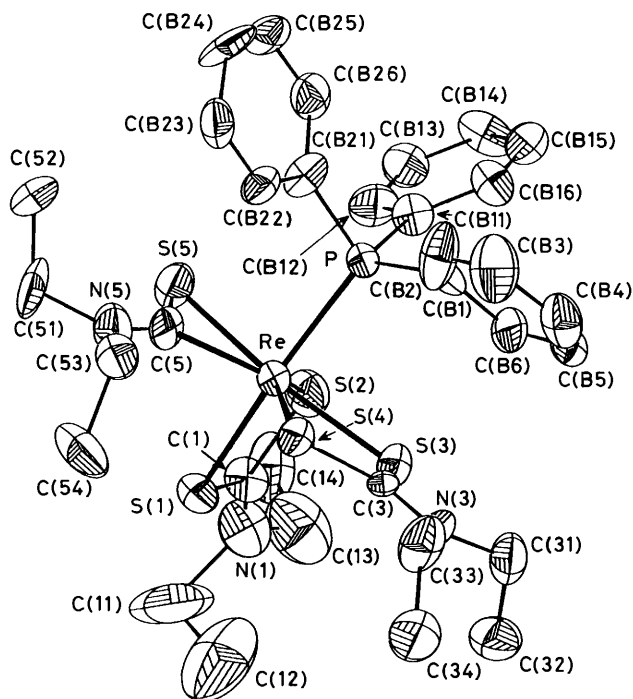
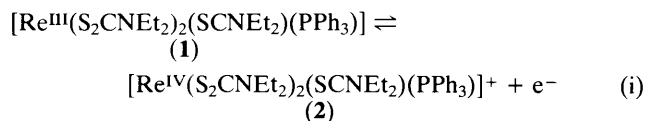


Figure 1. A view of the structure of the cation $[\text{Re}(\text{S}_2\text{CNET}_2)_2(\text{SCNET}_2)(\text{PPh}_3)]^+$. Selected bond lengths (\AA) and angles ($^\circ$): Re–P 2.476(7), Re–S(1) 2.426(7), Re–S(2) 2.425(7), Re–S(3) 2.449(8), Re–S(4) 2.475(8), Re–S(5) 2.398(7), Re–C(5) 2.098(23), C(5)–S(5) 1.605(24), C(5)–N(5) 1.297(36); P–Re–S(1) 170.4(3), P–Re–S(2) 98.7(2), P–Re–S(3) 88.9(3), P–Re–S(4) 91.2(3), P–Re–S(5) 89.0(3), P–Re–C(5) 97.4(6), S(1)–Re–S(2) 71.8(2), S(3)–Re–S(4) 69.5(3), C(5)–Re–S(5) 41.2(6), S(5)–C(5)–N(5) 137.4(21).

$(\text{SCNET}_2)(\text{PPh}_3)]\text{ClO}_4$ (2).[‡] Recrystallization from hot ethanol gave deep purple needle crystals.

The structure of the complex cation (2) is shown in Figure 1. § The co-ordination geometry of the rhenium atom is best described as a distorted pentagonal bipyramid. The triphenylphosphine ligand occupies an axial position and the η^2 -C,S-thiocarbamoyl group [C(5) and S(5)] is in an equatorial position. Both the dithiocarbamate ligands are bidentate; one provides equatorial [S(2)] and apically co-ordinated [S(1)] sulphur atoms and the other provides two equatorial sulphur atoms [S(3) and S(4)]. The bond lengths and angles in both η^2 -SCNET₂ and S₂CNET₂ groups in (2) are normal.^{2,3}



[‡] Satisfactory elemental analytical figures were obtained for (1) and (2). The i.r. (KBr disc) spectrum of (2) exhibits bands corresponding to $\nu(\text{C}=\text{N})$ of S₂CNET₂ at 1510 cm⁻¹ and $\nu(\text{C}=\text{N})$ of SCNET₂ at 1570 cm⁻¹.

§ *Crystal data:* C₃₃H₄₅ClN₃O₄PREs₅, $M = 960.68$, orthorhombic, space group P2₁2₁2₁, $a = 16.906(2)$, $b = 22.601(3)$, $c = 10.389(2)$ \AA , $U = 3970(1)$ \AA^3 , $Z = 4$, $D_c = 1.61$ g cm⁻³, $\mu(\text{Cu}-K\alpha) = 95.4$ cm⁻¹, crystal dimensions 0.1 × 0.1 × 0.2 mm. Data were collected at 20 °C with a Rigaku AFC-5 diffractometer using graphite monochromated Cu-K α radiation; 3590 unique data were collected, of which 2636 with $F_o > 3\sigma(F_o)$ were used in the analysis. The structure was solved by Patterson techniques and refined to final R and R_w values of 0.076 and 0.069. All programs used were from the UNICS-Osaka package. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

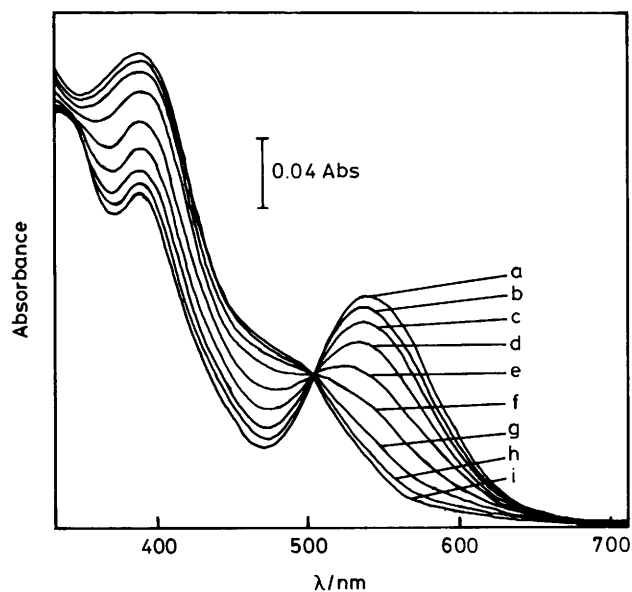


Figure 2. Sequential absorption spectra obtained during a spectro-potentiostatic experiment on 2.1 mm $[\text{Re}(\text{S}_2\text{CNET}_2)_2(\text{SCNET}_2)(\text{PPh}_3)]$ in 0.1 M tetrabutylammonium perchlorate/acetonitrile with a platinum optically transparent thin-layer electrode. Applied potentials in V are as follows: a, -0.485; b, -0.655; c, -0.685; d, -0.710; e, -0.735; f, -0.760; g, -0.785; h, -0.815; i, -0.985.

Cyclic voltammetric measurements at a platinum disc electrode in acetonitrile containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte show that (1) undergoes a reversible oxidation with $E^\circ = -0.74$ V,[¶] and that (2) undergoes a reversible reduction with $E^\circ = -0.74$ V. Figure 2 illustrates the spectra recorded during the spectro-potentiostatic⁵ oxidation of the complex (1). The Re^{III} complex has an absorption maximum at 390 nm with a shoulder at 472 nm; the Re^{IV} complex oxidized at -0.485 V exhibits maxima at 338, 387, and 537 nm, consistent with those for the complex (2). An isosbestic point is observed at 500 nm, which indicates that a clean interconversion between the two components of the redox couple, (1) and (2), occurs without concomitant ligand loss, according to equation (i). These electrochemical results suggest that (1) retains the same geometry as (2).

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[¶] All potentials reported here are with respect to E° of the ferrocenium/ferrocene couple.