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The Synthesis and Structure of [Re($SCH_2CH_2SCH_2CH_2CH_2SCH_2CH_2S$)($PPh_3$)(NNCOPh)], a Rhenium–Thiolato Complex Incorporating a Benzoyldiazenido-unit

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Although there has been intense interest in the chemistry of molybdenum and iron with thiolate ligands, the elements of Group VII have only recently received systematic attention [1, 2]. A series of oxo-dithiolato-complexes of technetium and rhenium have been described [3]. More recently, synthetic and structural studies of the incorporation of small molecules into the rhenium–thiolate framework [Re(SR)$_n$] have appeared [4–7]. As part of our systematic study of the characteristics of sulfur-ligated rhenium, we have prepared the first example of a rhenium–thiolate complex incorporating a diazenido-functionality, –NNR. Diazenido-complexes are of some interest as intermediates in the abiological reduction of coordinated dinitrogen [8] and have been extensively investigated as probes for the properties of sulfur-ligated metal ions [9].

Reaction of the six coordinate benzoyldiazenido-chelate (O,N) complex [$ReCl_2(PPh_3)_2$(NNCOPh)] [10] with a variety of tetradentate ligands of the general type $HSCH_2XCH_2CH_2CH_2XCH_2CH_2SH$ (X = S or NR) [11, 12] results in chelate ring opening to produce species of the general type [Re($SCH_2CH_2XCH_2CH_2CH_2XCH_2CH_2S$)($PPh_3$)(NNCOPh)]. When X = S, recrystallization from methylene chloride–ether solution produced yellow-orange crystals. The infrared spectrum of this material exhibits characteristic bands at 1636, 1580 and 1490 cm^{-1}, assigned to μ(CO) and μ(NN), respectively. The ^{1}H NMR spectrum shows no evidence of protonation of the coordinated diazenido-residue.

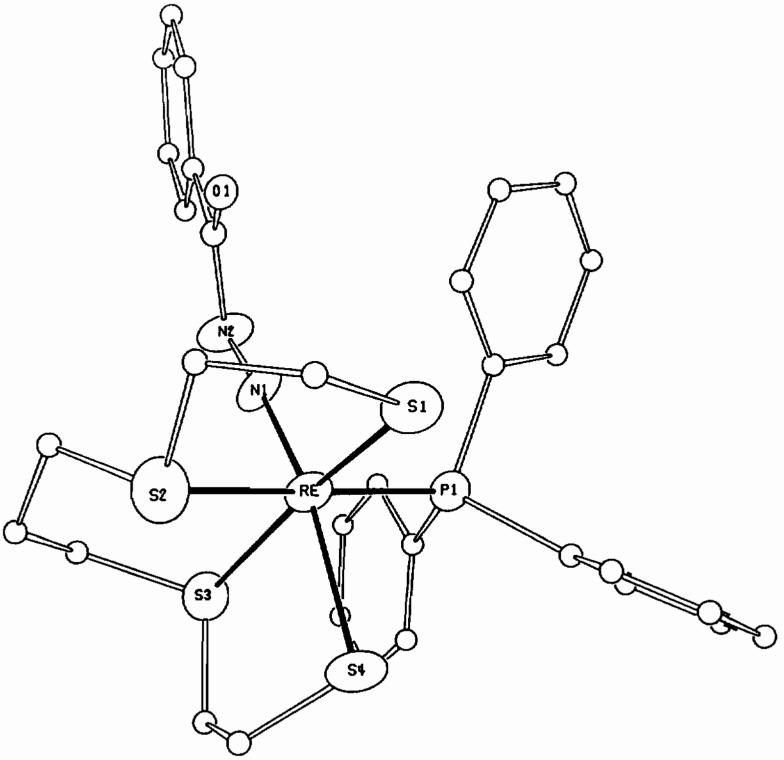

Fig. 1. ORTEP view of the structure of [Re($SCH_2CH_2SCH_2CH_2CH_2SCH_2CH_2S$)($PPh_3$)(NNCOPh)] showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Re–P, 2.414(4); Re–S(1), 2.354(4); Re–S2, 2.432(5); Re–S3, 2.483(4); Re–S4, 2.466(5); Re–N(1), 1.776(12), N(1)–N(2), 1.267(17); N(2)–C, 1.37(2); P–Re–S(1), 91.7(1); P–Re–S(2), 176.1(2); P–Re–S(3), 93.9(1); P–Re–S(4), 91.5(2); P–Re–N(1), 88.1(4); S(1)–R–S(2), 84.5(2); S(1)–Re–S(3), 169.7(1); S(1)–Re–S(4), 90.3(2); S(1)–ReN(1), 104.3(4); S(2)–Re–S(3), 89.7(2); S(2)–Re–S(4), 87.7(4); S(2)–Re–N(1), 93.6(4); S(3)–Re–S(4), 80.9(2); S(3)–Re–N(1), 84.5(4); S(4)–Re–N(1), 165.4(4).

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Crystal data: space group $P2_1/c$, $a = 11.804(2)$ Å, $b = 12.529(2)$ Å, $c = 21.448(3)$ Å, $\beta = 89.39(1)^\circ$, $V = 3171.8(2)$ Å^3, to give $D_c = 1.69$ g/cm^3 for $Z = 4$ (MoK_α radiation). Structure solution and refinement was based on 2981 reflections with $F_0 \geqslant 6\sigma(F_0)$ to give a conventional R factor of 0.068 with a goodness of fit of 1.58.

An ORTEP view of the molecule is presented in Fig. 1, showing the atom-labelling scheme and summarizing selected bond lengths and angles. The overall geometry of the rhenium is distorted octahedral, with the tetradentate ligand providing two *cis*-thiolato and two *cis*-sulfido donors while the phosphorus donor of the PPh_3 group and the α-nitrogen of the benzoyldiazenido-unit complete the coordination. The *cis*-orientation of the thiolate donors is unusual; linear tetradentate ligands with terminal thiolato-functionalities have generally assumed a *trans* thiolate configuration [13]. In fact, the *trans* thiolate arrangement is characteristic of most pseudo-octahedral structure of the types [$ML_2(SXXS)$], [$ML_2(SX)_2$] and [$ML_4(SR)_2$] (where X represents a nitrogen donor group), with the exception of certain rare instances where severe steric constraints impose *pseudo-cis* thiolate geometry [14].

A consequence of the *cis*-thiolate geometry is to dispose the thiolato-donor S(4) *trans* to the diazenido-unit. This orientation is most unusual as thiolate donors are generally disposed *cis* to strongly π-bonding groups, such as oxo- or diazenido-functionalities, although our recent structural studies reveal that diazenido groups permit greater structural flexibility than that allowed by the oxo-donors [15].

The strong *trans*-influence of the diazenido-group is evident in the Re–S(4) distance of 2.466(5) Å, a bond length considerably longer than the range of 2.32–2.37 Å generally observed for Re–thiolate interactions. In fact, the Re–S(4) bond distance is *ca.* 0.1 Å longer than the Re–S(1) thiolate bond length and on the order of the Re–thioether distances, Re–S(2) and Re–S(3), which are unexceptional for this type of interaction.

The Re–NNR moiety exhibits structural features common to linear metal–diazenido units. The Re–N(1) and N(1)–N(2) distances are short, suggesting extensive delocalization and multiple-bonding throughout the unit, an observation confirmed by the virtual planarity of the entire Re–$NNCOC_6H_5$ grouping. The observed geometry is consistent with the eighteen-electron rule, which constrains the ligand to function as a three electron donor and adopt the linear geometry.

The title complex may be synthesized in near quantitative amounts, and we are pursuing the reaction chemistry of this complex, particularly the protonation of the diazenido group and substitution reactions at the phosphine site.

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