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Rhenium Complexes with Sterically-Hindered Thiolate Ligands. The Structures of $[ReO(SC_6H_2Me_3)_4]^-$ and a Complex with an Unexpected Cation, $[Ph_3PSC_6H_3Pr_2^i][ReO(SC_6H_3Pr_2^i)_4]\cdot 1.5CH_3CH_2OH$

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We have recently initiated a research program to explore the coordination chemistry of sterically hindered thiolato-ligands. These are capable of stabilizing low-coordination numbers in monomeric complexes as they do not permit thiolato-bridging or undergo C–S bond cleavage to give sulphido-bridged oligomers. The coordinatively unsaturated species should be capable of interacting with small molecules thereby providing complexes relevant to sulfur-ligated active sites of certain metallo-enzymes. We have described elsewhere the chemistry of sterically hindered thiolates with molybdenum and tungsten oxo- and carbonyl complexes [1], and molybdenum and rhenium nitrosyl species [2]. There have also been reports of the complexes of related thiolates with iron[3], ruthenium and osmium [4], and cobalt and copper [5]. Here we report some new rhenium complexes with a variety of small molecules coordinated in conjunction with bulky thiolate ligands.

In an earlier publication we reported the reaction of $[ReOCl_3(PPh_3)_2]$ with excess thiophenylate anion in methanol to give the anion $[ReO(SPh)_4]^-$ as a tetraphenylphosphonium salt [6]. The thiols 2,4,6-trimethylthiophenol (TMTH), 2,6-diisopropylthiophenol (DIPTH) and 2,4,6-triisopropylthiophenol (TIPTH) react analogously despite large steric pressures to give $[ReO(TMT)_4]^-$ (**1**), $[ReO(DIPT)_4]^-$ (**2**), and $[ReO(TIPT)_4]^-$ (**3**)† isolated as the tetraphenylphosphonium and triethylammonium salts. Attempts to determine the structures of the $(PPh_4)^+$ salts of (**2**) and (**3**) were thwarted by disorder problems. However, the structure of (**1**), was determined‡ and we sought to systematize the effects of increasing thiolate bulk on coordination geometry, particularly with respect to the regular square pyramidal geometry displayed by the sterically innocent parent species $[ReO(SPh)_4]^-$ [7].

Suitable brownish-red crystals of (**1**) were obtained from dichloromethane–methanol, and the structure of the anion is shown in Fig. 1 together with selected bond lengths and angles. The geometry about the rhenium atom in $[ReO(TMT)_4]^-$ is distorted significantly from the square pyramidal coordination reported for the analogous unhindered complex $[ReO(SPh)_4]^-$ [7]. The coordination polyhedron has the rhenium atom displaced from the best plane through the four sulfur atoms 0.71 Å towards the apical oxygen atom. An analysis of shape-determining dihedral angles reveals that the angle formed by the intersection of the S1S2S3 and S2S3S4 planes is 13.6°, a considerable distortion from the coplanarity required for idealized square pyramidal geometry [8].

The stable purple complex $[Re(SPh)_3(MeCN)(PPh_3)]$ is prepared in high yield from $[FeCl_3(MeCN)(PPh_3)_2]$ and excess thiophenylate anion in acetonitrile [6]. Under the same conditions DIPTH gives $[Re(DIPT)_3(MeCN)(PPh_3)]$ (**4**) as a green crystalline complex. The co-existence of the bulky thiolates and triphenyl phosphine within the coordination sphere is surprising, but the presence of bound PPh_3 is confirmed by a ^{31}P resonance at about −122 ppm (free PPh_3 is −145 ppm). However, (**4**) is much less stable than its thiophenylate analogue, and attempted recrystallization from dichloromethane-ethanol in air gave a bright-red crystalline complex of empirical formula $[ReO(DIPT)_5(PPh_3)]$ (**5**). The presence of a medium intensity IR band at ~960 cm^{-1} suggested that Re=O may be present as $[ReO(DIPT)_4]^-$. This was verified by an X-ray crystal structure§ of (**5**) which revealed $[ReO(DIPT)_4]^-$ with the unexpected cation $[Ph_3PSC_6H_3Pr_2^i]^+$.

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†Satisfactory elemental analysis (C,H,N,S) were obtained for all new complexes.

‡Crystal Data for $[HNEt_3][ReO(SC_6H_2Me_3)_4]$, (**1**): Space Group $P2_1/n$, a = 12.988(3) Å, b = 16.387(3) Å, c = 21.336(4) Å, $\alpha = \gamma = 90°$, β = 102.78(1)°, V = 4428.4(10) $Å^3$ to give D_{calc} = 1.332 g/cm^3 for Z = 4. Structure solution based on 3407 reflections with $I_o > 3\sigma(I_o)$, R = 0.056, R_w = 0.054. Goodness of fit = 1.79.

§Crystal Data for $[Ph_3P{-}SC_6H_3Pr_2^i][ReO(SC_6H_3Pr_2^i)_4]\cdot 1.5CH_3CH_2OH$, (**5**): Space Group $P\bar{1}$, a = 14.295(2) Å, b = 14.620(5) Å, c = 19.689(4) Å, α = 86.97°(1), β = 77.15°(1), γ = 84.60°(1), V = 3992.31 $Å^3$ to give D_{calc} = 1.252 g/cm^3 for Z = 2. Structure based on 1813 reflections with $I_o > 3\sigma(I_o)$, R = 0.074, R_w = 0.067. Goodness of fit = 1.33. The 1.5 ethanols showed extensive disorder, and were included in the final refinement.

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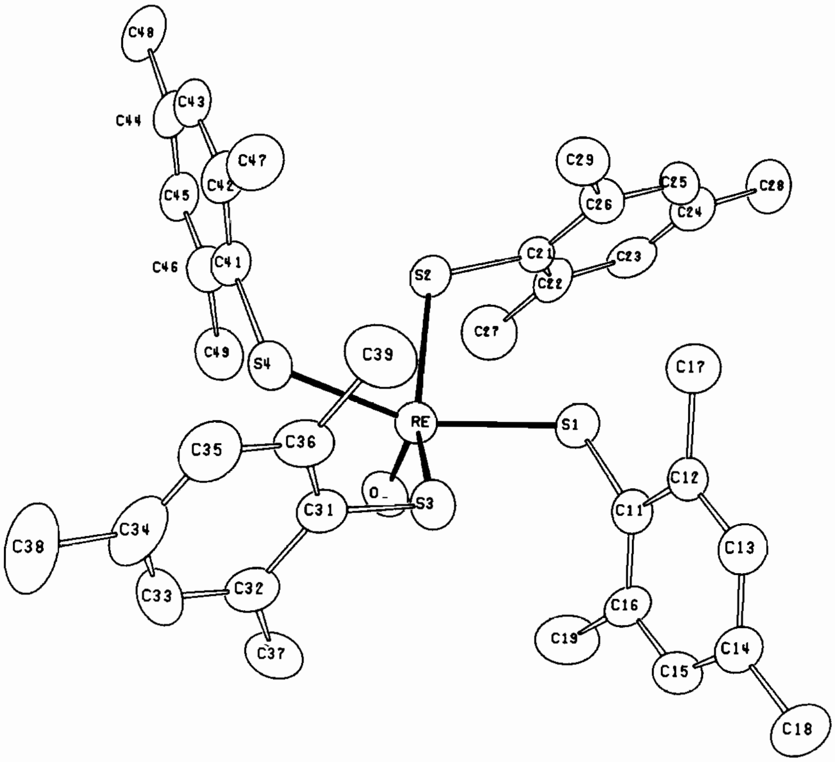

Fig. 1. ORTEP diagram of the $[ReO(TMT)_4]^-$ anion of (1). Selected bond distances (Å) and angles (deg): Re–S1, 2.339(4); Re–S2, 2.319(4); Re–S3, 2.322(4); Re–S4, 2.356(4); Re–O, 1.65(1); S1–Re–S2, 85.7(1); S3–Re–S4, 87.0(1); S1–Re–S3, 83.8(1); S2–Re–S4, 83.1(1); S2–Re–S3, 137.8(1); S4–Re–S1, 151.4(1); S1–Re–O, 105.5(4); S2–Re–O, 113.3(4); S3–ReO, 108.9(4); S4–Re–O, 103.1(4).

The structures of the anion and cation are shown in Fig. 2 together with relevant bond lengths and angles.**

Although we had anticipated that by replacing the methyl substituents of (**1**) with bulkier isopropyl-groups in the *ortho*-positions we would further distort the square based pyramid towards the trigonal bipyramidal limit, the analysis of shape-determining dihedral angles revealed close approximation to the square-pyramidal limit. The fold angles along the basal plane bisector S2–S3, that is, the dihedral angle between S1S2S3 and S2S3S4, is 5.4°, compared to values of 3.8° and 13.6° for $[ReO(SPh)_4]^-$ and (**1**), respectively. This observation suggests that the distortion from idealized square pyramidal geometry may originate as a result of intermolecular and crystal packing effects, rather than intramolecular ligand steric congestion.

Cations of the type $[R_3P{-}SAr]^+$ can be prepared by a variety of methods including the reaction of tertiary phosphine with diaryl disulphides [9]. The formation of (**5**) requires oxygen and is accompanied by the formation of $[Ph_3PSC_6H_3Pr_2{}^i][ReO_4]$. This suggests that the cation originates from disulphide interacting with free PPh_3 both being formed during the oxidation of (**4**) by oxygen. Although not previously encountered in our work, the formation of such cations may complicate reactions of thiolates with tertiary phosphine containing precursors. The phosphorous–sulfur bond length of 2.11 Å approximates the sum of their covalent radii suggesting that structure **I**, with the positive charge localized on the phosphorous atom, is the major contributing resonance structure.

**The Re–O group is disordered about the plane generated by the four sulfur atoms. Re′ is present at 10% occupancy and has been included in the final stages of refinement. The conventional R factor drops from a value of 0.071 to the final value of 0.053 as a consequence of including the disordered Re′ atom. The image of oxo-atom is also found on the final difference Fourier map but corresponds to a value of 0.6 $e/Å^3$ on a scale when a carbon atom is 5.5 $e/Å^3$. The disordered O′ atom has not been included in the refinement since there is no significant effect on the R factor ($R = 0.053$ with O′ included).

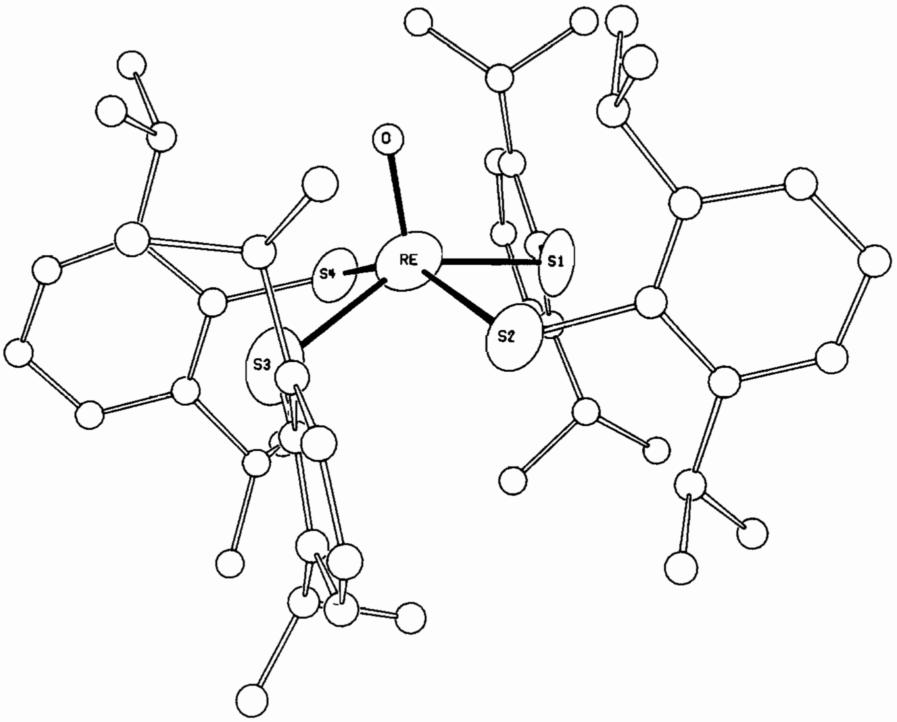

Fig. 2A. ORTEP diagram of $[ReO(DIPT)_4]^-$ anion with relevant bond lengths (Å) and bond angles (deg). Re–S1, 2.33(1); Re–S2, 2.36(1); Re–S3, 2.34(1); Re–S4, 2.38(1); Re–O, 1.70(2); S1–Re–S2, 83.7(4); S2–Re–S3, 86.3(4); S3–Re–S4, 83.4(4); S4–Re–S1, 86.2(4); S1–Re–S3, 142.8(4); S2–Re–S4, 149.2(4); S1–Re–O, 108.4(10); S2–Re–O, 106.1(9); S3–Re–O, 108.8(10); S4–Re–O, 104.7(9).

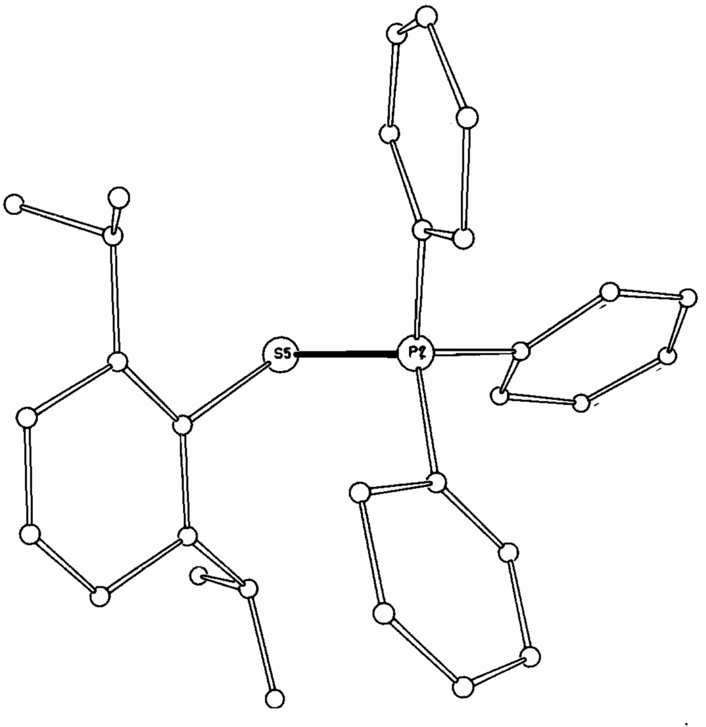

Fig. 2B. ORTEP diagram of the unexpected cation $[Ph_3P–S–C_6H_3Pr_2{}^i]^+$ with relevant bond lengths (Å) and bond angles (deg): P–S5, 2.11(2); P–C51, 1.74(4); P–C61, 1.78(3); P–C71, 1.85(4); S–C81, 1.85(4); S5–P–C51, 102.0(1); S5–P–C61, 113.0(1); S5–P–C71, 112.0(1); P–S5–C81, 100.0(1); C51–P–C61, 104.0(2); C61–P–C71, 112.0(2); C71–P–C51, 113.0(2).

$R_3\overset{+}{P}{-}SAr$ $\qquad$ $R_3P{=}\overset{+}{S}Ar$

I $\qquad$ **II**

Although (4) is relatively unstable, the deep violet complex $[Re(TIPT)_3(MeCN)_2]$ is readily prepared from K_2ReCl_6 and excess TIPT anion in refluxing MeCN, and can be recrystallized in air. The acetonitrile molecules can be replaced stepwise by CO to give $[Re(TIPT)_3(CO)_2]^-$ (ν(C–O) = 1965 cm^{-1}). The single CO stretch suggests that the latter complex is almost certainly isostructural with $[Mo(TIPT)_3(CO)_2]^-$ with *trans* CO ligands and three thiols in the equatorial sites of the trigonal bipyramid.

Previous attempts to prepare rhenium phenylimido or nitrido complexes with thiophenylate ligands invariably led to the formation of $[ReO(SPh)_4]^-$ [6]. However, the sterically hindered thiols DIPTH and TIPTH permit the isolation of the first stable crystalline thiolato complexes with both these nitrogen ligands. Thus $[ReCl_3(NPh)(PPh_3)_2]$ [10] reacts with the thiolate anions in methanol to give brown $[Re(NPh)(SAr)_4]^-$ (SAr = DIPT or TIPT). The nitrido complex $[FeCl_2(N)(PMe_2Ph)_3]$ [11] reacts under similar conditions to give yellow $[Re(N)(SAr)_2(PMe_2Ph)_2]$.

These results serve to reinforce our contention that sterically demanding thiolate ligands behave quite differently from simple unencumbered aromatic thiols and permit the isolation of low coordination number species capable of interacting with small molecules.*

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*Tables of atomic coordinates available upon request (6 pages).