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Five-co-ordinate Rhenium Thiolato-complexes: the Preparations and Structures of $[ReO(SPh)_4]^-$, $[Re(SPh)_3(MeCN)(PPh_3)]$ and $[Re(NPPh_3)(SPh)_4]$

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Although there has been intense recent interest in the chemistry of molybdenum and to some extent, tungsten, with sulphur ligands, elements in Groups V and VII have received scant attention. As part of our studies of the binding characteristics of sulphur-ligated metal ions [1] we have prepared the first examples of rhenium complexes of monodentate thiolates. A series of oxo-dithiolato-complexes of technetium and rhenium were described recently [2].

The Re(V) oxo-complex $[ReOCl_3(PPh_3)_2]$ reacts in refluxing methanol with an excess of aryl thiolate anion, to give a clear brownish solution. The complexes $[Ph_4P][ReO(SAr)_4]^-$ (Ar = C_6H_5, p-MeC_6H_4, C_6F_5, C_6Cl_5) can then be precipitated by the addition of $[Ph_4P]Br$. The thiolate anion is generated by addition of triethylamine in an amount equivalent to the thiol. The complexes all show an intense band in the range 950–990 cm^{-1} assigned to ν(Re=O). Conductivity measurements over a range of concentrations and the equivalence of the *p*-Me groups suggest the anions are monomeric. They are therefore analogous to the molybdenum(V) complexes $[MoO(SAr)_4]^-$ [3], and probably share the same square pyramidal structure with apical oxo-group. The complexes undergo irreversible one electron oxidations and two electron reductions in acetonitrile at a Pt electrode with $[Bu_4N][BF_4]$ as support electrolyte. Full details will be reported elsewhere.

The complexes $[ReO(SAr)_4]^-$ react with excess PPh_3 in refluxing MeCN to give the purple Re(III) complexes $[Re(SAr)_3(MeCN)(PPh_3)]$ (A). The complexes (A) can also be prepared by reaction of $[ReCl_3(MeCN)(PPh_3)_2]$ with arylthiolate anions.

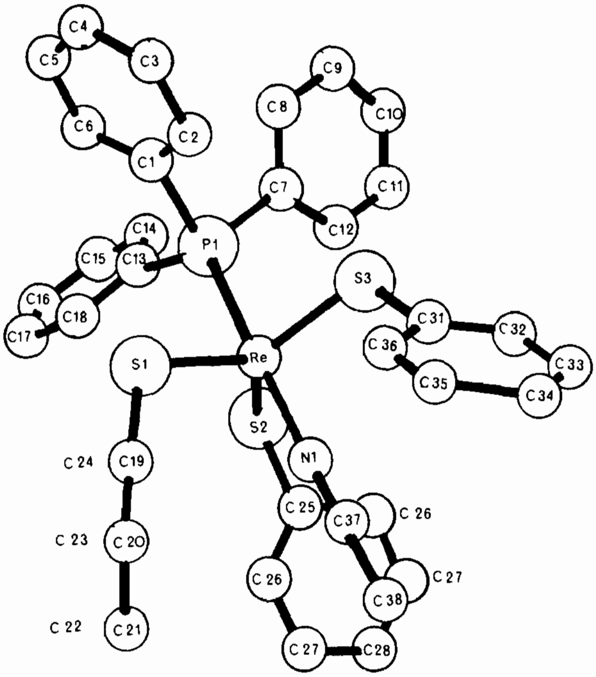

Fig. 1. An ORTEP representation of the structure of $[Re(SPh)_3(MeCN)(PPh_3)]$ showing the atom labelling scheme. Important bond lengths (Å) and angles (°): RE–S1, 2.248(7); Re–S2, 2.555(6); Re–S3, 2.264(7); Re–P1, 2.351(6); Re–N1 2.07(2). N1–C37, 1.16(3), C37–C38, 1.49(4). S1–Re–S2, 118.7(3); S1–Re–S3, 117.2(2); S2–Re–S3, 124.0(2); S1–Re–P1, 90.0(2); S1–Re–N1, 93.9(6); S2–Re–P1, 87.4(2); S2–Re–N1, 89.4(6);S3–Re–P1, 89.0(2); S3–Re–N1, 90.6(6).

The X-ray crystal structure of the complex $[Re(SPh)_3(MeCN)(PPh_3)]$ was undertaken, and an ORTEP representation of the structure appears in Fig. 1 with some important bond lengths and angles. The complex consists of discrete monomeric trigonal pyramidally co-ordinated Re atoms. The thiolato-sulphurs occupy the trigonal plane with the MeCN and PPh_3 groups in axial positions. An interesting feature of the complex is the disposition of all the thiolato-aryl groups away from the PPh_3 group, to provide a molecular cavity containing the MeCN group. These aryl groups provide a steric constraint to the ligands which can occupy the apical site *trans* to the PPh_3 group. Thus small linear molecules such as CO will readily replace the MeCN to give $[Re(SPh)_3(CO)(PPh_3)]$ (ν(CO) = 1962 cm^{-1}) whereas ligands such as acetylene which bind side-on cannot be accommodated.

The nitrido-complex $[ReNCl_2(PPh_3)_2]$ reacts with an excess of arylthiolate anion in acetonitrile under reflux to give a yellow solution from which no well

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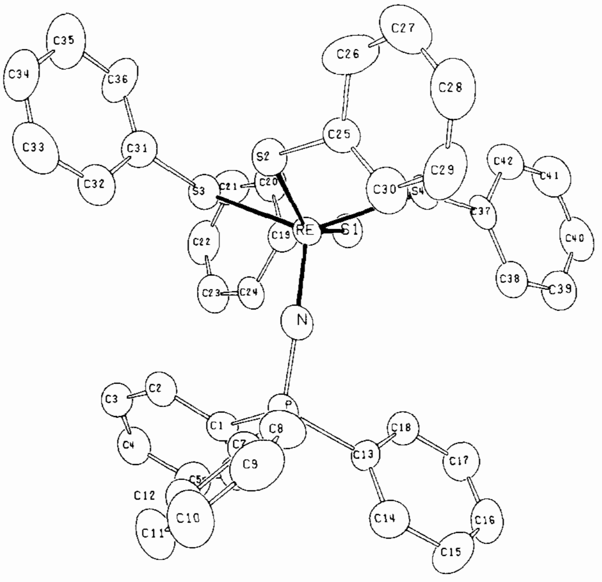

Fig. 2. An ORTEP representation of the structure of [Re($NPPh_3$)($(SPh)_4$] showing the atom labelling scheme. Important bond lengths (Å) and angles (°): Re–N, 1.743(7); Re–S1, 2.337(2); Re–S2, 2.323(3); Re–S3, 2.318(2), Re–S4, 2.330(3). P–N, 1.634(9); P–Cl, 1.787(2); N–Re–S1, 107.1(3); N–Re–S2, 197.4(3); N–Re–S3, 109.5(3); N–Re–S4, 109.4(3); S1–Re–S2, 145.4(1); S1–Re–S3, 83 7(1); S1–Re–S4, 84.3(1); S2–Re–S3, 84.6(1); S2–Re–S4, 84.6(1); S3–Re–S4, 141.1(1); Re–N–P, 163.1(6).

characterised products were isolable. However subsequent aerial oxidation generated a dark green-brown solution from which the complex [Re($NPPh_3$)($(SPh)_4$] was isolated in about 20% yield. The complex shows an intense i.r. band at 1120 cm^{-1} assigned to ν(P=N)

As it was initially difficult to distinguish this i.r band from ν(P=O) of a ligated $Ph_3P=O$ andX-ray crystal structure determination was undertaken. An ORTEP representation of the structure is shown in Fig. 2 together with some important bond lengths and angles. The geometry about Re is essentially square-pyramidal with an apical $NPPh_3$ group. The Re–N and N–P distances of 1.743(7) and 1.634(9) Å are very close to the corresponding values found in [$RuCl_3(NPEt_2Ph)(PEt_2Ph)_2$] [4] and indicate considerable Re–N and P–N multiple bonding.

The role of oxygen in the preparative reaction is unclear, but it may involve oxidisation of a [ReN($(SPh)_4$]$^{2-}$ intermediate to the neutral Re(VII) nitride [ReN$(SPh)_4$]. Here the nitride would be expected to have considerable electrophilic character and react with the PPh_3 expelled into solution to give the observed phosphinimato-complex.

Acknowledgements

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References

1 J. R. Dilworth, J. P. Hutchinson and J. A. Zubieta, *J Am. Chem. Soc*, *104,* 365 (1982).
2 A. Davison, C. Orvig, H. S. Trop, M. Sohn, B. de Pamphilis and A. G. Jones, *Inorg Chem*, *19,* 1978 (1980).
3 I. W Boyd, I. G. Dance, K. S. Murray and A G. Wedd, *Austr. J. Chem.*, *31,* 279 (1978).
4 F. L. Phillips and A. Skapski, *Chem. Commun.*, 49 (1974).