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Trigonal Bipyramidal Compounds of Technetium with a Tetradentate Umbrella Ligand

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We have established the tendency of Tc(III) to form stable five-coordinate, 14-electron complexes with sterically hindered arene thiolate ligands [1, 2]. Structural characterization of a number of the members of the series $Tc(SAr)_3(L)(L')$ (SAr = 2,3,5,6-tetramethylbenzenethiolate or 2,4,6-triisopropylbenzenethiolate; L, L′ = CO, MeCN, CNR, PEt_3 and/or py) has shown that these compounds consistently exhibit trigonal bipyramidal geometry in which the thiolates are bound in the equatorial plane and the axial sites are capped by the π-accepting ligands L and L′. We have now designed a chelating 'umbrella' ligand which provides technetium with the three thiolate ligands and one of the axial π-acceptors, while leaving the fifth coordination site open for ligand exchange.

Tris-(*o*-thiophenyl)phosphine (PS3)** was prepared in 79% overall yield by reacting *o*-bromothioanisole with n-BuLi followed by PCl_3, according to the procedure of Dyer and Meek [4]. Reduction with $Na/NH_3(l)$ afforded the free trithiol. ^{1}H NMR data for PS3 ($CDCl_3$): δ5.22 (d, 3H); 7.92 (m, 3H); 8.22 (m, 3H); 8.39 (m, 3H); 8.52 (m, 3H). Reaction of this chelate with $(n\text{-}Bu_4N)[TcOCl_4]$ and a proton sponge in acetonitrile yields a dark-green intermediate which reacts readily with isopropylisonitrile. Chromatography on silica/$CHCl_3$ provides the orange compound Tc(PS3)(i-PrNC) (**1**) in 68% yield. ^{1}H

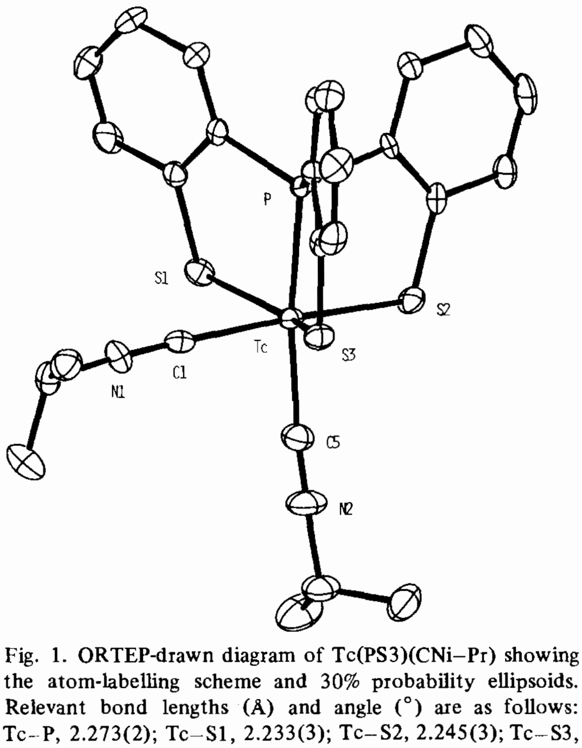

Fig. 1. ORTEP-drawn diagram of Tc(PS3)(CNi–Pr) showing the atom-labelling scheme and 30% probability ellipsoids. Relevant bond lengths (Å) and angle (°) are as follows: Tc–P, 2.273(2); Tc–S1, 2.233(3); Tc–S2, 2.245(3); Tc–S3, 2.231(2); Tc–C1, 2.06(1); C1–N, 1.14(1); P–Tc–C1, 176.1(3); P–Tc–S1, 85.66(8); P–Tc–S2, 85.75(8); P–Tc–S3, 85.35(8); C1–Tc–S1, 94.9(3); C1–Tc–S2, 97.3(3); C1–Tc–S3, 91.0(3); S1–Tc–S2, 118.9(1); S1–Tc–S3, 119.1(1); S2–Tc–S3, 120.2(1).

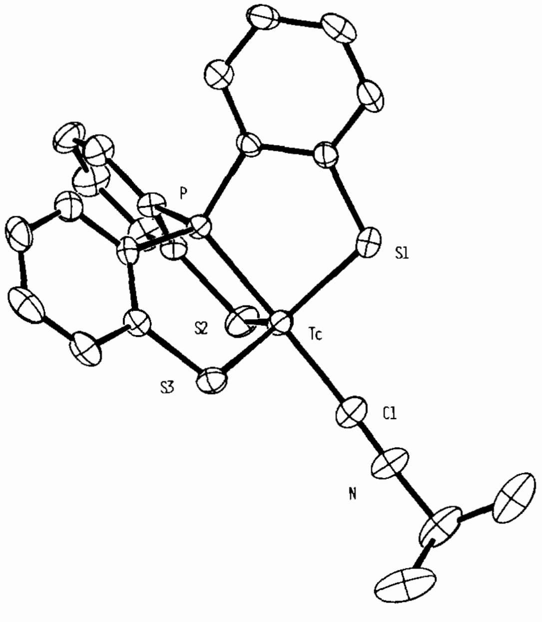

Fig. 2. ORTEP-drawn diagram of $Tc(PS3)(CNi\text{–}Pr)_2$ showing the atom-labelling scheme and 30% probability ellipsoids. Relevant bond lengths (Å) and angles (°) are as follows: Tc–P, 2.290(2); Tc–S1, 2.390(2); Tc–S2, 2.310(2), Tc–S3, 2.328(2); Tc–C1, 2.081(7); Tc–C5, 2.058(8); C1–N1, 1.152(8); C-5–N2, 1.150(9); P–Tc–C1, 99.2(2); P–Tc–C5, 172.5(2); P–Tc–S1, 82.81(6); P–Tc–S2, 84.65(6); P–Tc–S3, 84.52(6); C1–Tc–S1, 76.5(2); C1–Tc–S2, 175.3(2); C1–Tc–S3, 76.6(2); C5–Tc–S1, 101.8(2); C5–Tc–S2, 88.6(2); C5–Tc–S3, 94.3(2); S1–Tc–S2, 106.46(7); S1–Tc–S3, 147.91(7); S2–Tc–S3, 106.46(7).

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**An alternative preparation of this compound was recently reported [3].

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NMR data for **1** ($CDCl_3$): δ1.70 (d, 6H); 4.54 (m, 1H); 7.28 (m, 3H); 7.37 (m, 3H); 7.55 (dd, 3H); 8.38 (t, 3H). Addition of excess isonitrile to a solution of the orange compound causes the metal to bind a second isonitrile ligand forming the dark-blue, paramagnetic compound Tc(PS3)(i-PrNC)$_2$ (2). This reaction is easily reversed by removal of the excess isonitrile.

Both the five-coordinate (**1**) and the six-coordinate (**2**) complexes were structurally characterized by X-ray crystallography. X-ray data for **1**, $TcPS_3NC_{22}H_{19}$: monoclinic, $a = 10.3541(8)$, $b = 13.2274(6)$, $c = 16.437(1)$ Å; $\beta = 90.855(6)°$, space group $= P2_1/c$, $Z = 4$, final $R = 0.049$, $R_w = 0.057$. Compound 2, $TcPS_3N_2C_{26}H_{26}$: orthorhombic, $a = 18.896(1)$, $b = 13.2815(8)$, $c = 10.3823(6)$ Å; space group $= Pna2_1$, $Z = 4$, final $R = 0.044$, $R_w = 0.048$. The ORTEP-drawn diagrams as well as some relevant bond distances and angles are shown in Figs. 1 and 2, respectively. In the trigonal bipyramidal compound **1**, the umbrella ligand fits snugly over the technetium, leaving the metal only 0.172 Å out of the plane defined by the three sulfur atoms. Incorporation of the second isonitrile ligand imposes pseudo-octahedral geometry on compound **2**. Interestingly, the two technetium isonitrile bond distances in **2** hardly differ ($\Delta = 0.023$ Å) despite the fact that one of the isonitrile ligands is quite labile. These two structures illustrate the flexibility of the PS3 ligand as it opens up to accommodate a second isonitrile ligand. Such flexibility has been observed previously with the related ligand tris-(*o*-diphenylarsinophenyl)arsine [5].

References

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