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Preliminary communication

CYCLOPENTADIENYL PENTAFLUOROPHENYLTHIOLATE COMPLEXES OF MOLYBDENUM AND TUNGSTEN AS NOVEL POLYDENTATE LIGANDS OF THALLIUM(I); DYNAMIC NMR STUDIES AND CRYSTAL STRUCTURES OF TWO DERIVATIVES $[MoTl(SC_6F_5)_2L_2Cp]$ ($L = SC_6F_5$ or CO)

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Summary

New bimetallic complexes $[MTl(SC_6F_5)_2L_2Cp]$ ($L = SC_6F_5$, M = Mo (**1a**), W (**1b**); L = CO, M = Mo (**4**)) are characterised; crystal structures of **1a** and **4** show unusual polydentate coordination of thallium(I) by $[Mo(SC_6F_5)_2L_2Cp)]^-$ and var. temp. ^{19}F NMR studies, supported by conductivity measurements and cation exchange, indicate restricted rotation of C_6F_5 groups and reversible decoordination of Tl^+ in more polar solvents.

Recent studies in our laboratories of paramagnetic halogeno- and thiolato-dienemolybdenum(III) complexes resulted in the isolation of small quantities of a novel molybdenum-thallium complex $[MoTl(SC_6F_5)_4Cp]$ ($Cp = \eta^5\text{-}C_5H_5$) (**1a**) of undetermined structure [1]. We now report more efficient routes to **1a** and to related Mo–Tl and W–Tl complexes and the characterisation of these complexes by dynamic NMR and X-ray diffraction studies. These studies reveal the ability of the thallium(I) to coordinate reversibly to metal(II) and metal(IV) organometallic anions.

Synthetic investigations, summarized in Scheme 1, establish that the reaction of **2** with $Tl(SC_6F_5)$ affords the Mo^{II}–Tl^{I} adduct **4** in 78% yield via complex **3**, and this undergoes total CO substitution to give the Mo^{IV}–Tl^{I} adduct **1a** in 30% yield as a

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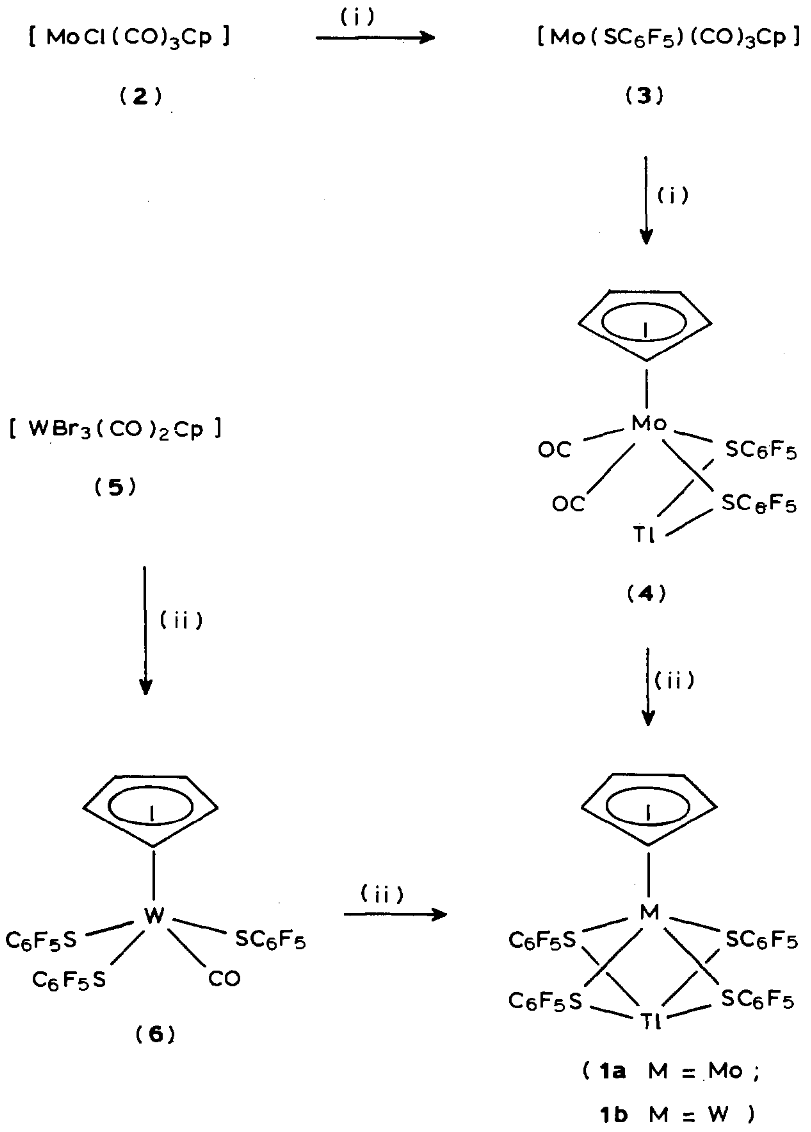

SCHEME 1. (i) $TlSC_6F_5$ in Et_2O, 20°C. (ii) 5/1 excess of $TlSC_6F_5$ in CH_2Cl_2, 20°C.

result of Tl^I promoted oxidation *. Since **1b** is not accessible from analogous W^{II} complexes an alternative synthetic route was developed utilising the W^{IV} complex **5**: this readily produces **1b** in 33% yield via a novel 16e thallium-free intermediate **6**.

X-ray diffraction studies of **1a** and **4** have established the presence of Tl^I unusually coordinated by organometallic ligands $[CpMo(SC_6F_5)_2L_2]$ ($L = SC_6F_5$

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* Satisfactory elemental analyses have been obtained for **1a**, **1b**, **4**, **6** and **7**; additionally, preliminary X-ray diffraction studies of **6** and **7** confirm the structures; several isomers of **6** are in equilibrium in solution: IR ($CDCl_3$): $\nu(CO)$ 1940 cm^{-1}; ^1H NMR ($CDCl_3$, 20°C); δ 5.28, 5.57, 5.65 and 6.46 (s, C_5H_5) ppm.

(**1a**); CO (4)), see Fig. 1 and 2. The crystal structure of complex **1a** * consists of discrete molecules of [MoTl$(SC_6F_5)_4$Cp] in which the thallium lies above the square-plane defined by the four sulphur atoms whereas complex **4** forms part of an infinite chain held together by interactions between the thallium and the two sulphurs on a neighbouring symmetry-related mononuclear species ($\frac{1}{2}+x$, $-\frac{1}{2}+y$, $1-z$). Thus, the thallium in **4** attains a coordination similar to that in **1a**. In both **1a** and **4** the extended Tl–Mo distances (3.402(3) and 3.518(1) Å, respectively) suggest minimal metal–metal interaction [2]. The observed intramolecular Tl–S distances in **4** are typicaly of Tl^I–S complexes and clusters [3], though the Tl–S bonds in **1a**, which are on average longer by 0.25 Å, probably reflect severe steric congestion within the complexes. Moreover, as illustrated in Fig. 1b and 2b the thallium atom also makes a series of intramolecular non-bonding "soft" contacts with neighbouring *ortho*-fluorines of the C_6F_5 groups which not only influence the C_6F_5 conformations but, presumably, also increase the stability of the complexes [4].

From Fig. 1b it is apparent that the organometallic ligand in **1a** comprises a cavity, defined by the MoS_4 unit and by four *ortho*-fluorine atoms, which effectively encapsulate Tl^I. The ^{19}F NMR spectra of **1a** at −79°C in $C_6D_5CD_3$ ($\delta(CCl_3F)$: −123.5 (J(TlF) 3630 Hz; 4 *o*-F), −126.2 (4 *o*-F) −148.8 (4 *p*-F, J(FF) 21 Hz), −155.2 (4 *m*-F), −157.6 (4 *m*-F) ppm) and **1b** −80°C in CD_2Cl_2 ($\delta(CCl_3F)$: −128.2 (J(TlF) 3506 Hz; 4 *o*-F), −131.5 (4 *o*-F), −154.6 (4 *p*-F), −160.8 (4 *m*-F) −162.6 (4 *m*-F) ppm) are consistent with the solid state structure determined for **1a** and reveal significant spin–spin coupling interactions between $^{203/205}Tl$ and one of the two sets of four equivalent *ortho*-fluorine atoms. At higher temperatures (e.g. ca 72°C for **1a** in $C_6D_5CD_3$) fluxional behaviour exchanges the two *ortho*-F environments with retention of an average Tl–F coupling; in $(CD_3)_2CO$ related spectra with one mean Tl–F coupling to all equivalent *ortho*-F atoms are observed at −60 to −70°C whereas at ambient temperature this coupling is lost giving rise to one simple *ortho*-fluorine resonance. We interpret this behaviour in terms of an initial C_6F_5 rotation followed at higher temperature by reversible decoordination of Tl^+ from the organometallic unit. The latter effect clearly occurs more readily in the more polar solvent where cation solvation is better. Although polymeric in the solid state, complex **4** exhibits almost identical VT ^{19}F NMR spectra (e.g. in

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* *Crystal data for* **1a**: $C_{29}H_5F_{20}MoS_4Tl$, orange plates, orthorhombic, a 14.388(4), b 14.841(4), c 14.904(4) Å, U 3182.5 Å^3, $Z=4$, D_c 2.675 g cm^{-3}, $F(000)=2424$, $\mu=59.0$ cm^{-1}. Intensity data collected on CAD4 diffractometer ($\omega-2\theta$ scans, $2<\theta<28°$, Mo-K_α radiation). Space group $Pn2_1a$ (non standard setting of No. 33) from successful structure solution and refinement. After full-matrix least square refinement [7], R and R_w were 0.052 and 0.050 respectively for 1472 data with $I>2\sigma(I)$ and anisotropic temperature factors for Tl, Mo and S only. *Crystal data for* **4**: $C_{19}H_5F_{10}MoO_2S_2Tl$, yellow plates, monoclinic, a 17.210(6), b 10.598(3), c 12.109(4) Å, $\beta=99.86°$, U 2176.0 Å^3, $Z=4$, D_c 2.50 g cm^{-3}, $F(000)=1520$, μ 83.2 cm^{-1}, space group $P2_1/a$. Intensity data collected on a CAD4 diffractometer ($\omega-2\theta$ scans, $2<\theta<25°$, Mo-K_α radiation). After refinement [7] (full-matrix least squares, anisoptropic temperature factors for all non-hydrogen atoms) R and R_w were 0.051 and 0.058 respectively for 2210 reflections with $I>2\sigma(I)$. The X-ray data for **1a** and **4** were corrected for absorption (DIFABS [7]), in addition to the usual Lorentz and polarisation effects.

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

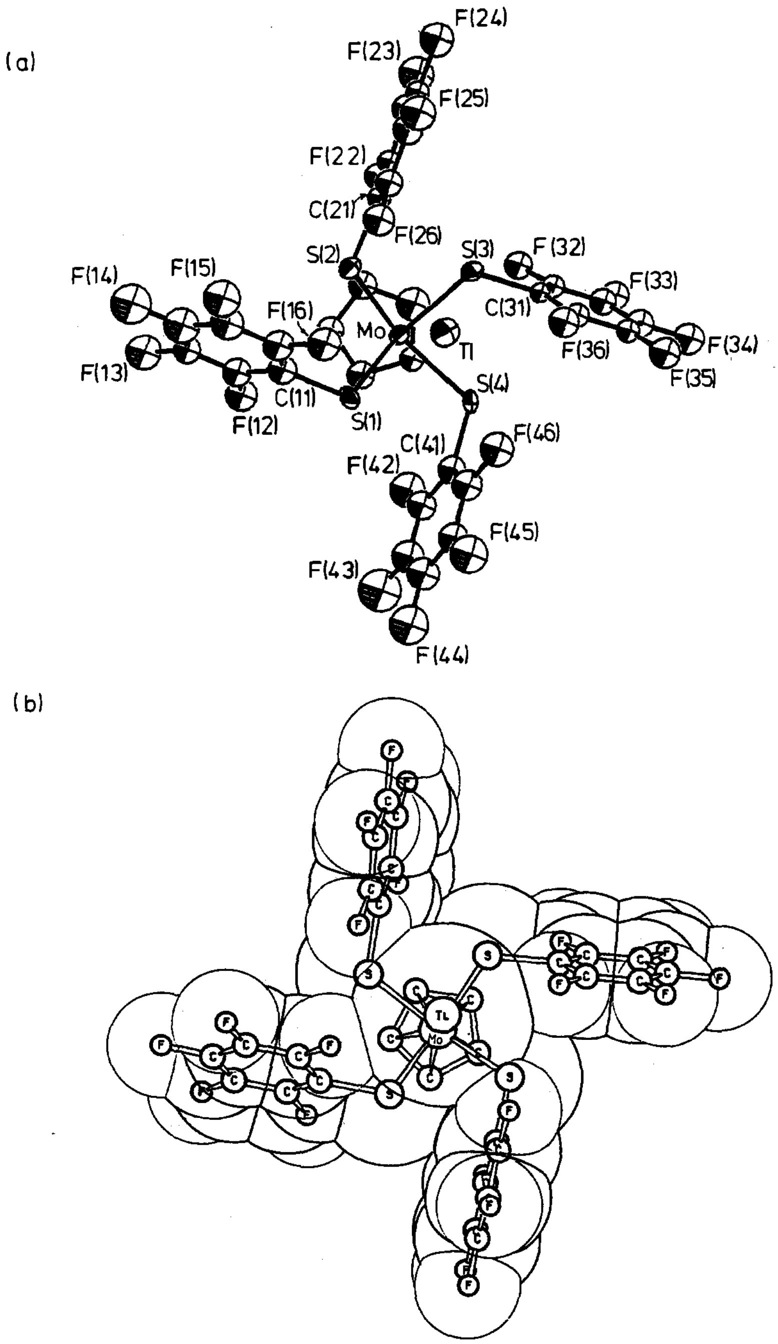

Fig. 1. Crystal structure of **1a**: (a) ORTEP diagram (30% ellipsoids). The hydrogen atoms and numbering for the carbon atoms of the cyclopentadienyl group C(1)–C(5)) and those bonded to fluorine in the C_6F_5 groups have been omitted for clarity. (b) SCHAKAL space-filling diagrams. Important interatomic distances: Tl–Mo 3.402(3), Tl–S(1) 3.276(9), Tl–S(2) 3.342(7), Tl–S(3) 3.200(8), Tl–S(4) 3.292(8), Mo–S(1) 2.402(8), Mo–S(2) 2.425(8), Mo–S(3) 2.420(9), Mo–S(4) 2.447(8), Tl–F(16) 2.978(1), Tl–F(26) 3.144(1), Tl–F(36) 3.080(1), Tl–F(26) 3.144(1), Tl–F(36) 3.080(1), Tl–F(46) 3.046(1) Å.

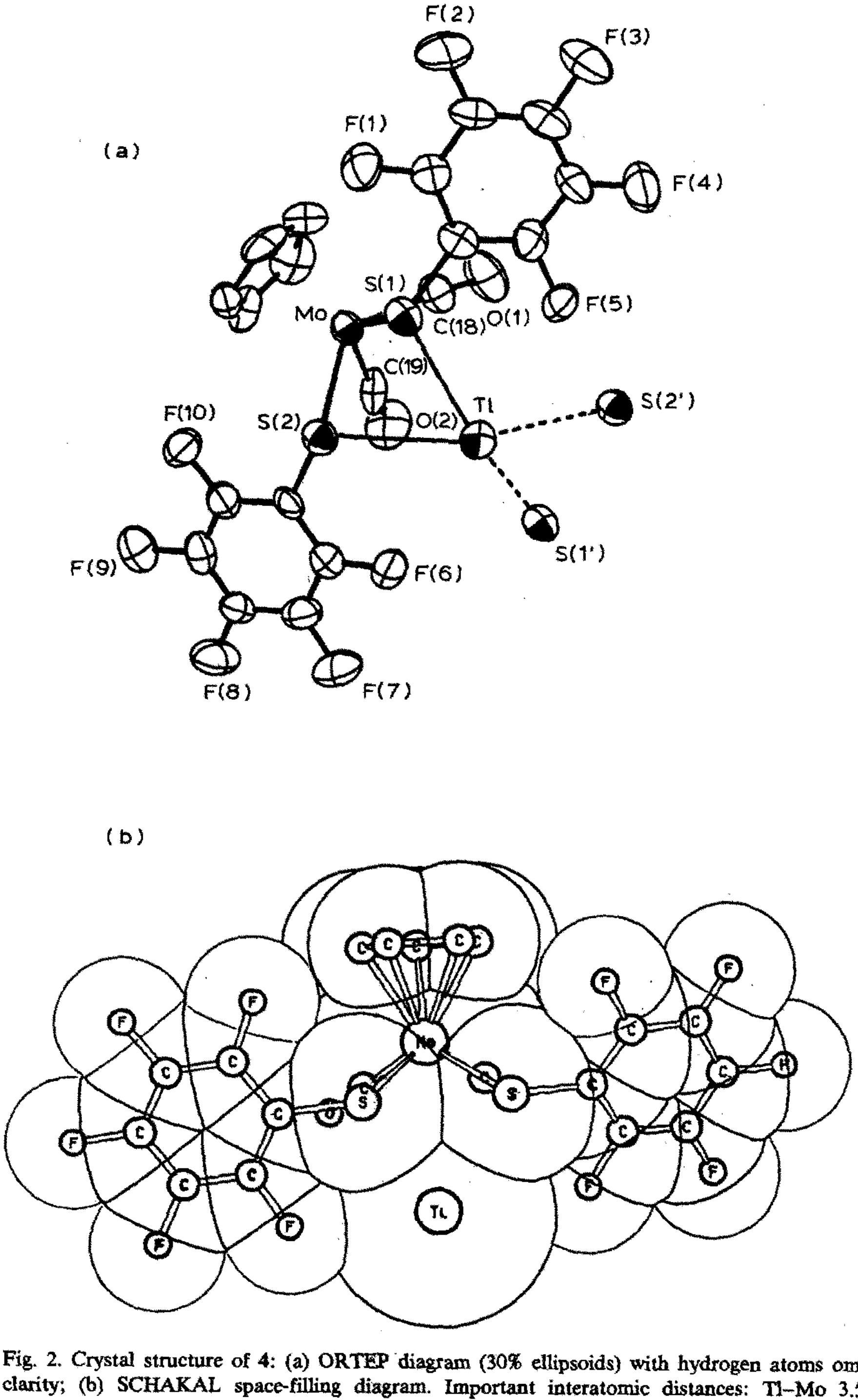

Fig. 2. Crystal structure of 4: (a) ORTEP diagram (30% ellipsoids) with hydrogen atoms omitted for clarity; (b) SCHAKAL space-filling diagram. Important interatomic distances: Tl–Mo 3.5180(10), Tl–S(1) 2.998(4), Tl–S(2) 3.032(4), Mo–S(1) 2.538(4), Mo–S(2) 2.530(4), Mo–C(13) 1.981(16), Mo–C(19) 1.978(18), Tl–F(5) 3.099(9), Tl–F(6) 3.090(10), Tl–S(1′) 3.772(3), Tl–S(2′) 3.333(3) Å.

$C_6D_5CD_3/Et_2O$ at −100°C: δ (CCl_3F): −130.2 (J(Tl-F) 3375 Hz, 2 *o*-F), −130.7 (2 *o*-F), −158.74 (2 *p*-F), 161.9 (2 *m*-F) −163.72 (2 *m*-F) ppm) to those of complexes **1a** and **1b** implying that, in solution, discrete monomers exist which undergo similar dynamic processes. Investigations by ^{205}Tl NMR, potentially a useful probe for these processes, were rather uninformative; no resonance was found for **1a** and both **1b** and **4** give single broad bands in acetone (r.t.; **1b** δ ($TlNO_3$, Θ_{ref} 57.683833 MHz) −60.5 ppm ($\Delta\omega\frac{1}{2}$ ~ 1000 Hz); **4** +828 ppm ($\Delta\omega\frac{1}{2}$ ~ 600 Hz)) or CH_2Cl_2 (r.t.; **4** δ + 1225 ppm ($\Delta\omega\frac{1}{2}$ ~ 1000 Hz)).

Appreciable ionisation of complex **1a** in acetone is supported by conductivity measurements (Λ 78 Ω^{-1} cm^2 mol^{-1}; 10^{-3} M, 25°C).Conductivity data for complex **4** in acetone (Λ 6 − 14 Ω^{-1} cm^2 mol^{-1}; $10 - 0.8 \times 10^{-3}$ M, 25°C), although indicating less dissociation [5], also support ionization to a kinetically significant extent to explain the VT ^{19}F NMR results. Metathetical replacement of Tl^+ in complexes **1a**, **1b** or **4** by non-coordinating cations $[PPN]^+$ or $[NR_4]^+$ was also carried out, giving for example $[PPN]^+[Mo(SC_6F_5)_4Cp]^-$ (**7**) (Λ ~ 73 Ω^{-1} cm^2 mol^{-1}; 10^{-3} M, 25°C, acetone).

These results draw attention to the ability of organometallic anions to function as polydentate ligands towards thallium(I) and potentially towards other metal ions. This and the fact that coordination is reversible illustrates that anions of this type may have potential as selective sequestering agents towards various metal ions, a possibility we are actively investigating. In this respect two important features are the size and geometry of the coordination sites on the organometallic anion and a crucial factor in **1** and **4** is the availability of a vacant capping position on the square plane distal to the cyclopentadienyl ligand. Accordingly we note that a halogen ligand occupies this site in trihalides **5** whereas in coordinatively and electronically unsaturated thiolate complexes **1** and the intermediate tungsten complex **6** the site is vacant. This may be related to the ability of thiolate ligands [6] to stabilise coordinative unsaturation by sulphur → metal π-donation.

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