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Synthesis and nuclear magnetic resonance studies of molybdenum and tungsten thiolate complexes

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Reactions of $[WCl_3(CO)_2(\eta^5\text{-}C_5H_5)]$ with $Tl[SC_6F_4H\text{-}4]$ and $[WBr_3(CO)_2(\eta^5\text{-}C_5H_5)]$ with Tl[SR] (R = Ph or $C_6H_4Me\text{-}4$) in dichloromethane gave tungsten(IV) compounds $[W(SPh)_3(CO)(\eta^5\text{-}C_5H_5)]\cdot 0.25CH_2Cl_2$ **1a**, $[W(SC_6H_4Me\text{-}4)_3(CO)(\eta^5\text{-}C_5H_5)]$ **1b** and $[W(SC_6F_4H\text{-}4)_3(CO)(\eta^5\text{-}C_5H_5)]$ **1c**, respectively. Reaction of $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ with 2 molar equivalents of $Tl[SC_6F_4H\text{-}4]$ in diethyl ether gave a mixture of $[Mo(SC_6F_4H\text{-}4)(CO)_3(\eta^5\text{-}C_5H_5)]$ **2** and $Tl[Mo(SC_6F_4H\text{-}4)_2(CO)_2(\eta^5\text{-}C_5H_5)]$ **3**. The photochemical reaction of $Tl[Mo(SC_6F_4H\text{-}4)_2(CO)_2(\eta^5\text{-}C_5H_5)]$ and $(SC_6F_4H\text{-}4)_2$ in tetrahydrofuran (thf) afforded $Tl[Mo(SC_6F_4H\text{-}4)_4(\eta^5\text{-}C_5H_5)]$ **4a** whilst $[WBr_3(CO)_2(\eta^5\text{-}C_5H_5)]$ and 5 equivalents of $Tl[SC_6F_4H\text{-}4]$ gave $Tl[W(SC_6F_4H\text{-}4)_4(\eta^5\text{-}C_5H_5)]$ **4b**. These were converted into $[N(PPh_3)_2][M(SC_6F_4H\text{-}4)_4(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) on reaction with $[N(PPh_3)_2]Cl$. Reactions of $[W(SC_6F_4H\text{-}4)_3(CO)(\eta^5\text{-}C_5H_5)]$ with alkali-metal derivatives $M'[SC_6F_4H\text{-}4]$ in thf afforded $M'[W(SC_6F_4H\text{-}4)_4(\eta^5\text{-}C_5H_5)]$ (M′ = K **4c**, Rb **4d** or Cs **4e**). With M′ = Na the tetrathiolate complex was obtained as a thf solvate $Na[W(SC_6F_4H\text{-}4)_4(\eta^5\text{-}C_5H_5)]\cdot$thf **5**. Fluorine-19 NMR spectroscopy revealed that **1c** and **3–5** undergo several dynamic processes, *viz.* fluxional behaviour involving rotation/inversion of the $SC_6F_4H\text{-}4$ groups. The spectra of the thallium and caesium derivatives {and ^{133}Cs spectra in the case of $Cs[M(SC_6F_4H)_4(\eta^5\text{-}C_5H_5)]$} in addition show coupling between the metal M′ and four of the *o*-fluorines of the $SC_6F_4H\text{-}4$ groups at low temperatures providing evidence for reversible co-ordination between the M'^+ cation and the organometallic anion. This behaviour is solvent dependent, occurring more readily in more polar solvents.

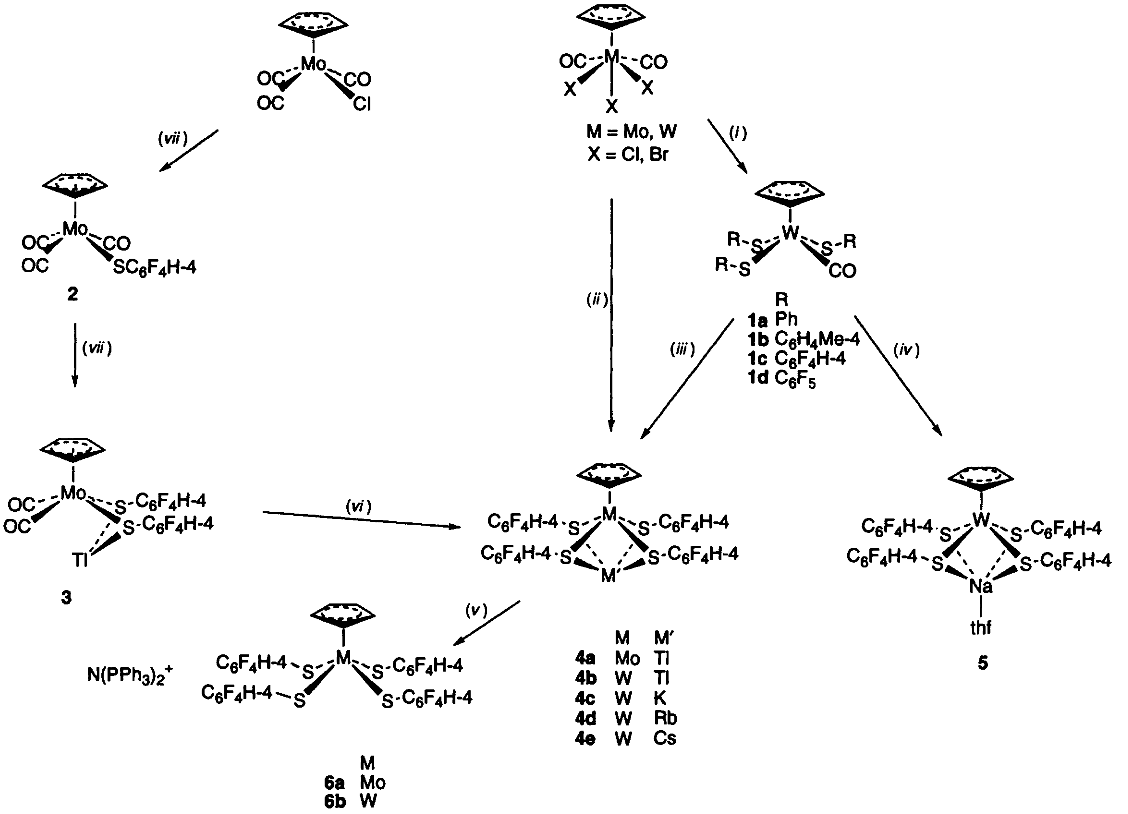
Recently we reported the syntheses and dynamic NMR studies of molybdenum[1] and tungsten[2] derivatives $Tl[M(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]$ (M = Mo or W). X-Ray diffraction studies of the molybdenum complex and the derivative $[N(PPh_3)_2][Mo(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]$ revealed that the organometallic anion contains a cavity defined by the transition metal, four primary donor sites (sulfur) and four secondary sites (four *o*-fluorines of the C_6F_5 groups) which can encapsulate a Tl^+ ion. Variable-temperature ^{19}F NMR spectra of $Tl[M(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]$ show solvent-dependent coupling between these four fluorines and $^{203/205}Tl$. At higher temperatures dissociation of the Tl^+ leads to loss of coupling, accompanied by the onset of fluxional motion involving the SC_6F_5 groups. We subsequently extended this work to the synthesis of SeC_6F_5 complexes[3] and alkali-metal derivatives $M'[M(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]$ (M′ = K, Rb or Cs) and tetrahydrofuran solvates $Li[M(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]\cdot 4$thf and $Na[M(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]\cdot$thf.[4] Interestingly we were able to demonstrate by dynamic ^{19}F and ^{133}Cs NMR spectroscopy that the anions $[M(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]^-$ are also able reversibly to co-ordinate to the Cs^+ ion in solution, whereas attempts to co-ordinate them to transition metals failed.[5] This contrasts with recent studies of interactions between metal ions and the Fe_3S_4 cluster of *Pyrococcus furiosus* ferredoxin where softer metals were found to be capable of co-ordination (presumably with the sulfide ligands) but Cs^+ was not.[6] These observations prompted us to extend our studies by varying the nature of the thiolate ligand substituents in this type of complex with a view to changing the donor characteristics of the sulfur atom and hence its co-ordination abilities. We now report the results of these studies which are summarised in Scheme 1.

Results and Discussion

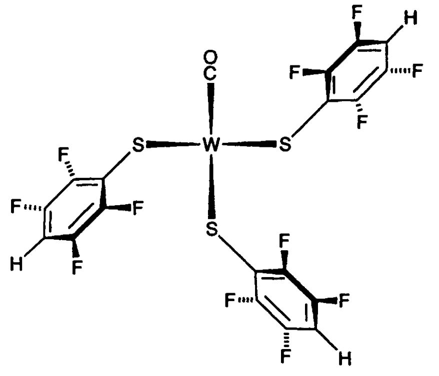
Initially we attempted to extend our previous work to thiolate derivatives containing stronger electron-donating groups in order to increase the basicity of the thiolate sulfurs and hence their donor capability. With this in mind $[WBr_3(CO)_2(\eta^5\text{-}C_5H_5)]$ and Tl[SPh] were allowed to react in dichloromethane and, after work-up from dichoromethane–light petroleum, dark green-brown crystals of $[W(SPh)_3(CO)(\eta^5\text{-}C_5H_5)]\cdot 0.25\,CH_2Cl_2$ **1a** were isolated and characterised. In an attempt to isolate $[W(SC_6H_4Me\text{-}4)_3(CO)(\eta^5\text{-}C_5H_5)]$ the reaction of $[WBr_3(CO)_2(\eta^5\text{-}C_5H_5)]$ with 3 $Tl[SC_6H_4\text{-}Me\text{-}4]$ in dichloromethane was also carried out and this gave a dark brown crystalline solid **1b** after work-up from dichoromethane–light petroleum. However, although the spectroscopic data for this compound are consistent with the formula given (see below), satisfactory analytical data were not obtained. The reaction of $[WCl_3(CO)_2(\eta^5\text{-}C_5H_5)]$ with a three-fold excess of $Tl[SC_6F_4H\text{-}4]$ similarly gave the analytically pure monocarbonyl $[W(SC_6F_4H\text{-}4)_3(CO)(\eta^5\text{-}C_5H_5)]$ **1c**.

Spectroscopic data for all three complexes are in accord with their proposed stoichiometry and structure. The IR spectra exhibit a single ν(CO) peak between 2020 and 2030 cm^{-1} which compares with 2030 cm^{-1} for the structurally characterised $[W(SC_6F_5)_3(CO)(\eta^5\text{-}C_5H_5)]$ **1d**.[2] These high values are in accord with the high oxidation state of the complexes, W^{IV}, and this is also reflected in the low-field chemical shift of the cyclopentadienyl group, *ca.* δ 5.5, in the ^1H NMR spectra. Interestingly, despite the poor analytical data, the spectrum of the $SC_6H_4Me\text{-}4$ derivative **1b** suggests a completely pure sample with appropriate integrated ratios for the C_5H_5 and C_6H_4Me peaks. In the case of the SPh derivative **1a** the presence of the dichloromethane solvate is indicated by ^1H NMR and analytical data. This was not observed with **1b** and **1c** although previously we found that $[W(SC_6F_5)_3(CO)(\eta^5\text{-}C_5H_5)]$ **1d** crystallised from dichloromethane–light petroleum as a dichloromethane solvate.[2]

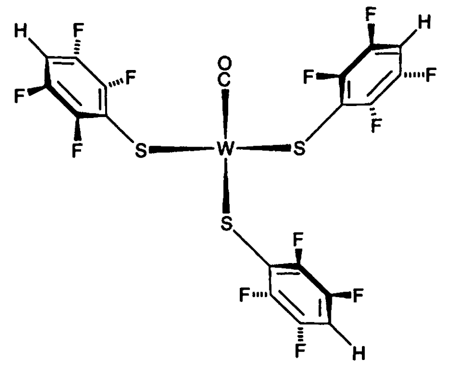
The structure of the SC_6F_5 derivative **1d** was reported previously and found to consist of a distorted four-legged piano-stool. The distortion consists of variations in the L–M–Ct angles (L = ligand, M = metal, Ct = centroid of the $\eta^5\text{-}C_5H_5$ ligand) which, in the case of the above complex, results in a value of 102.6° for the CO–M–Ct angle. Larger values are observed for the π-donor sulfurs, 110.2° for the *trans* SC_6F_5 group and a mean of 119.9° for the *cis* groups. This can be explained by assuming significant overlap between the filled metal d_{xy} highest occupied molecular orbital (HOMO) and the empty CO π* orbital. A wider ranging analysis of distortions in four-legged piano-stool molecules $[ML_4(\eta^5\text{-}C_5H_5)]$ is in full agreement with this suggestion.[7] Of more significance for the present case, the thiolate substituents, as with $[Mo(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]^-$, adopt a particular orientation, that illustrated in **A**. However, two other isomeric forms are possible, **B** and **C**, and ^{19}F NMR studies of $[W(SC_6F_5)_3(CO)(\eta^5\text{-}C_5H_5)]$ revealed the presence of two forms at low temperatures. Since molecular graphics studies effectively preclude **C** on steric grounds, we proposed that the two forms are **A** and **B**. In the case of $[W(SC_6F_4H\text{-}4)_3(CO)(\eta^5\text{-}$



Scheme 1 (*i*) $3Tl[SR]$, CH_2Cl_2; (*ii*) $Tl[SC_6F_4H\text{-}4]$, CH_2Cl_2; (*iii*) $M'[SC_6F_4H]$, (M' = K, Rb or Cs), thf, R = $C_6F_4H\text{-}4$; (*iv*) $Na[SC_6F_4H\text{-}4]$, thf, R = $C_6F_4H\text{-}4$; (*v*) $[N(PPh_3)_2]Cl$, CH_2Cl_2, M' = Tl; (*vi*) $(SC_6F_4H\text{-}4)_2$, thf, *hv*; (*vii*) $Tl[SC_6F_4H\text{-}4]$, Et_2O



A



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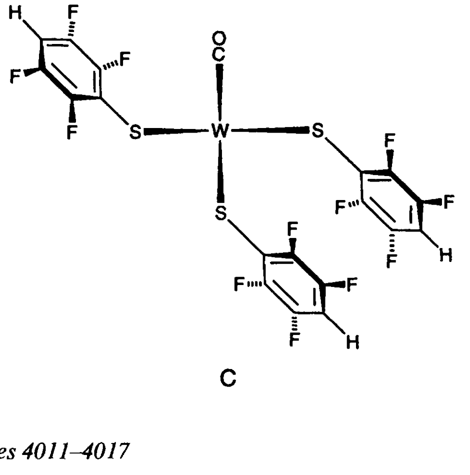


C

$C_5H_5)]$ **1c** the situation is more ambiguous since the ^{19}F NMR spectrum showed evidence of non-rigidity with two broad *and four sharp* peaks at 20 °C. If the SC_6F_4H groups undergo rapid rotation about the W–S and S–C bonds a set of *ortho* and *meta* peaks, ratio 2 : 1, would be observed whereas rotation about the S–C bonds only would give a set of *ortho* and *meta* peaks, ratio 2 : 1, for each isomer. Neither is consistent with the observed spectrum. High-temperature spectra were not obtained due to sample instability, but at lower temperatures all six peaks broaden and split to give a much more complex spectrum. Unfortunately this complexity, combined with the dispersion available at 188 MHz, prevents detailed conclusions from being reached. The use of the SC_6F_4H proton as a structural probe was similarly precluded by the complexity of the ^1H NMR signal at 200 MHz arising from coupling to two *o*- and two *m*-fluorines of the C_6F_4H ring. In the case of the equivalent SC_6F_5 derivative **1d** the *p*-fluorine resonances provided a simpler and more easily interpreted signal.[2] Consequently we are unable to reach any conclusions about isomerism and fluxional behaviour in complex **1c**. It is conceivable that the situation may be similar to that of **1d**, in which the two forms **A** and **B** undergo dynamic behaviour involving rotation of the the SR groups about the W–S and S–C bonds, but the data do not provide clear evidence for this.

It is interesting that tungsten(IV) derivatives of this type containing three terminal SR ligands can be synthesized since the sulfur in arenethiolate groups normally prefers to function in a bridging mode in organometallic derivatives. However, this appears to be less prevalent in carbonyl (cyclopentadienyl)-tungsten thiolates where even the monothiolate complexes $[W(SR)(CO)_3(\eta^5\text{-}C_5H_5)]$ exhibit reasonable stability. This is not the case with equivalent molybdenum derivatives which only resist dimerisation when electron-withdrawing CF_3 or C_6F_5 substituents are present on sulfur.[8] Interestingly however, simple tetrathiolate complexes of Mo^{IV} and W^{IV}, $[M(SBu^t)_4]$, have been isolated by Otsuka *et al.* and Schrock and co-workers[9] respectively, perhaps indicating that terminal ligands are more likely with higher-oxidation-state metals.

In an attempt to synthesize thallium derivatives $Tl[W(SR)_4(\eta^5\text{-}C_5H_5)]$, reactions of $[W(SC_6H_5)_3(CO)(\eta^5\text{-}C_5H_5)]$ with Tl[SPh] and $[W(SC_6H_4\text{-}Me\text{-}4)_3(CO)(\eta^5\text{-}C_5H_5)]$ with $Tl[SC_6H_4Me\text{-}4]$ were carried out. Unfortunately neither reaction produced tractable products and attention was therefore focused on derivatives of the $SC_6F_4H\text{-}4$ group which is, in electronic terms, more akin to the SC_6F_5 ligand employed successfully in previous work. The $SC_6F_4H\text{-}4$ analogues of known molybdenum SC_6F_5 derivatives were obtained from the reaction of $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ with 2 equivalents of $Tl[SC_6F_4H\text{-}4]$ which gave a mixture of $[Mo(SC_6F_4H\text{-}4)(CO)_3(\eta^5\text{-}C_5H_5)]$ **2** and $Tl[Mo(SC_6F_4H\text{-}4)_2(CO)_2(\eta^5\text{-}C_5H_5)]$ **3**. The former is presumably produced initially (see ref. 1) and undergoes further reaction with $Tl[SC_6F_4H\text{-}4]$ *via* CO substitution to give the thallium bis(thiolate) derivative. A more efficient route to **2** involves photolysis of $[\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$ and the disulfide $(SC_6F_4H\text{-}4)_2$ in toluene which gave $[Mo(SC_6F_4H\text{-}4)(CO)_3(\eta^5\text{-}C_5H_5)]$ in 61% yield.

The complex $[Mo(SC_6F_4H\text{-}4)(CO)_3(\eta^5\text{-}C_5H_5)]$ is a variant of a known structural type, *i.e.* a square-legged piano-stool,[10] and since it has similar spectroscopic features to previously characterised derivatives such as $[Mo(SCF_3)(CO)_3(\eta^5\text{-}C_5H_5)]$,[8] $[Mo(SeC_6F_5)(CO)_3(\eta^5\text{-}C_5H_5)]$[3] and $[Mo(SC_6F_5)(CO)_3(\eta^5\text{-}C_5H_5)]$[8] no further discussion is required. The spectroscopic properties of $Tl[Mo(SC_6F_4H\text{-}4)_2(CO)_2(\eta^5\text{-}C_5H_5)]$ are analogous to those of the SC_6F_5 and SeC_6F_5 derivatives reported earlier[1,3] showing two ν(CO) bands in the IR spectrum at 1953 and 1871 cm^{-1}. The ^{19}F NMR spectrum shows expected behaviour, *i.e.* a sharp *m*-fluorine resonance and a very broad *ortho* peak at room temperature in $CDCl_3$. Such behaviour has been observed with $Tl[Mo(SC_6F_5)_2(CO)_2(\eta^5\text{-}C_5H_5)]$ and is ascribed to thallium ion dissociation combined with perfluoroaryl group rotation and/or inversion at sulfur. Detailed low-temperature NMR studies of **3** were not carried out because of the limited stability of the complex in solution but a similar structure to that of the SC_6F_5 derivative is proposed.

The photochemical reaction of $Tl[Mo(SC_6F_4H\text{-}4)_2(CO)_2(\eta^5\text{-}C_5H_5)]$ with the disulfide $(SC_6F_4H\text{-}4)_2$ in thf solution subsequently gave the molybdenum(IV) derivative $Tl[Mo(SC_6F_4H\text{-}4)_4(\eta^5\text{-}C_5H_5)]$ **4a**. This route is not applicable to tungsten derivatives and $Tl[W(SC_6F_4H\text{-}4)_4(\eta^5\text{-}C_5H_5)]$ **4b** was obtained from the reaction of $[WBr_3(CO)_2(\eta^5\text{-}C_5H_5)]$ with 5 equivalents of $Tl[SC_6F_4H\text{-}4]$ in dichloromethane. The reaction probably proceeds *via* the monocarbonyl **1c**[2,3] but this possibility was not investigated. Both thallium derivatives were readily transformed into crystalline salts $[N(PPh_3)_2][M(SC_6F_4H\text{-}4)_4(\eta^5\text{-}C_5H_5)]$ (M = Mo **6a** or W **6b**) on reaction with $[N(PPh_3)_2]Cl$. The spectroscopic features of **6a** and **6b** are simpler and will be described first.

Proton and $^{31}P\text{-}\{^1H\}$NMR spectra of complexes **6a** and **6b** were recorded at ambient temperature only and show features (see Experimental section) in accord with the proposed structures with solvent-separated anions and cations. The ^{19}F NMR spectra were recorded in CD_2Cl_2 over the temperature range 20 to −90 °C. One set of relatively sharp *o*- and *m*-fluorine resonances is observed at room temperature but these broaden and collapse to give two sets of peaks at lower temperatures. Free energies of activation $\Delta G^\ddagger$ for the fluxional process (presumably $SC_6F_4H\text{-}4$ rotation and/or inversion) were estimated from the coalescence temperatures for both *ortho* and *meta* resonances and found to be $\Delta G^\ddagger_{221} = 40.3 \pm 0.5$, $\Delta G^\ddagger_{207} = 39.1 \pm 0.5$ kJ mol^{-1} for **6a** and $\Delta G^\ddagger_{234} = 42.5 \pm 0.5$, $\Delta G^\ddagger_{220} = 41.7 \pm 0.5$ kJ mol^{-1} for **6b**. These values compare with $\Delta G^\ddagger_{226} = 41.0 \pm 0.5$ or $\Delta G^\ddagger_{229} = 43.4 \pm 0.5$ kJ mol^{-1} for $[N(PPh_3)_2][M(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]$ (M = Mo or W, respectively).[5]

The observation of two sets of *o*- and *m*-fluorine resonances at low temperature is indicative of a preferred C_6F_4H orientation presumably that observed in the solid state for the SC_6F_5 derivative $[N(PPh_3)_2][Mo(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]$ as reported in earlier.[2] In four-legged piano-stool complexes such as $[M(SR)_3(CO)(\eta^5\text{-}C_5H_5)]$ and $[M(SR)_4(\eta^5\text{-}C_5H_5)]$ the orientation will be determined by the d orbital with which the π-donor orbital of the sulfur interacts.[2,10,11] Interaction with d_{xy} favours a structure with R directed away from the C_5H_5 ligand (*a*), whereas π bonding with d_{z^2} leads to an orientation (*b*) in the plane of the four SR ligands, see Fig. 1. The latter is found in the solid-state structures of both $[N(PPh_3)_2][Mo(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]$[2] and the thallium derivative $Tl[Mo(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]$[1] indicating a preference for π bonding with Mo d_{z^2} in both cases. Interestingly, however, $[Ta(SC_6H_5)_4(\eta^5\text{-}C_5H_4Me)]$ adopts a distorted piano-stool geometry which approaches a trigonal-bipyramidal structure in which two thiolates orientate so as to π donate to d_{xy} and the other two donate to d_{z^2}.[12] In complexes $[M(SR)_4(\eta^5\text{-}C_5H_5)]$ **4** (M = Mo or W) of the type reported here the preference for the observed orientation (*b*) can be attributed to the d-orbital configuration of the metal, *i.e.* d_{z^2} is empty and available for π donation from sulfur whilst the alternative orientation is precluded by the fact that d_{xy} is filled.

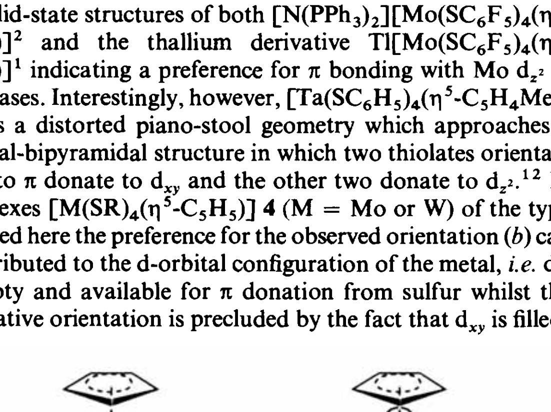


Fig. 1 The S→M π donation and thiolate orientation in $[M(SR)_4(\eta^5\text{-}C_5H_5)]$

The ^{1}H NMR spectra of Tl[M(SC$_6$F$_4$H-4)$_4$(η^5-C$_5$H$_5$)] (M = Mo **4a** or W **4b**) in CD$_2$Cl$_2$ exhibit the expected SC$_6$F$_4$H-4 proton multiplet and η^5-C$_5$H$_5$ singlet. Interestingly, however, when the spectra are recorded in CDCl$_3$, the latter in each case exhibits a doublet structure which is more clearly resolved when recorded at lower field strength, 80 MHz. Since this splitting is absent for the N(PPh$_3$)$_2$ derivatives we assume that the doublet is due to coupling of the cyclopentadienyl protons with the co-ordinated thallium with J(Tl–H) = 4.1, (**4a**) or 2.8 Hz, (**4b**). It is not clear why this is only observed in CDCl$_3$ although the influence of field strength may point to a linewidth effect. Close inspection of spectra taken in CD$_2$Cl$_2$ do suggest that the signal is broader than might be expected for a simple uncoupled singlet.

Variable-temperature ^{19}F NMR spectra were recorded for the thallium derivatives Tl[M(SC$_6$F$_4$H-4)$_4$(η^5-C$_5$H$_5$)] (M = Mo **4a** or W **4b**) between 20 and −90 °C in CD$_2$Cl$_2$ and reveal fluxional behaviour as expected with each showing broad *o*- and *m*-fluorine signals at 20 °C. These separate into two *ortho* and two *meta* signals below *ca.* −30 to −50 °C but with these complexes one of the *ortho* peaks is split into a doublet J(Tl–F) = 3510 (**4a**) or 3533 Hz (**4b**), providing evidence for co-ordination of the thallium ion. The structure of the complex at the low temperature is presumably that illustrated in Scheme 1, whilst the fluxional behaviour can again be ascribed to a combination of thiolate group rotation/inversion combined with reversible co-ordination of the thallium ion as described earlier[1,2] for the equivalent SC$_6$F$_5$ derivatives. Interestingly we note that neither of the SC$_6$F$_5$ derivatives Tl[M(SC$_6$F$_5$)$_4$(η^5-C$_5$H$_5$)] (M = Mo or W) showed a frozen spectrum in CD$_2$Cl$_2$, even at −90 °C. Moreover, the spectra of the SC$_6$F$_5$ derivatives do not 'freeze out' until *ca.* −80 °C in toluene. This either suggests that thallium co-ordination occurs more readily with SC$_6$F$_4$H-4 or merely reflects the effect of different frequency separations for the exchanging resonances. If the former is true it appears that even a relatively minor change in the thiolate substituent has a noticeable effect on the co-ordinating abilities of the anion.

In view of the apparent difference in the co-ordinating abilities of the SC$_6$F$_5$ and SC$_6$F$_4$H-4 derivatives [M(SR)$_4$(η^5-C$_5$H$_5$)]$^-$, towards Tl$^+$ it was of interest to prepare complexes with other metal ions. Recently we isolated alkali-metal salts of the tungsten anion [W(SC$_6$F$_5$)$_4$(η^5-C$_5$H$_5$)]$^-$ and unambiguously demonstrated that co-ordination of one of these, Cs$^+$, occurred in solution.[4] We therefore extended this work to related SC$_6$F$_4$H-4 complexes. These were obtained by the same synthetic strategy involving reaction of a monocarbonyl, in this case [W(SC$_6$F$_4$H-4)$_3$(CO)(η^5-C$_5$H$_5$)], with alkali-metal derivatives M'[SC$_6$F$_4$H-4] (M' = Na, K, Rb or Cs) in thf solution. In each case the reactants gave the desired products M'[W(SC$_6$F$_4$H-4)$_4$(η^5-C$_5$H$_5$)] **4c**–**4e** although with M' = Na the product **5** contained one molecule of thf of solvation which parallels our previous findings with the SC$_6$F$_5$ compound. Satisfactory elemental analyses were obtained for all complexes except the potassium derivative which, despite being spectroscopically pure, did not give acceptable carbon, hydrogen or sulfur analyses, even after repeated crystallisation.

The variable-temperature ^{19}F and ^{133}Cs NMR spectra of the caesium derivative **4e** were recorded in deuteriated acetone, dichloromethane and toluene. In acetone no evidence for Cs–F coupling was observed in the ^{19}F spectrum down to −80 °C, although fluxional behaviour involving the SC$_6$F$_4$H-4 groups which was rapid at 20 °C (two sharp fluorine peaks) was arrested below *ca.* −50 °C (four peaks). Similarly the ^{133}Cs spectrum exhibited an invariant singlet in deuteriated acetone over the range 0 to −80 °C which, in conjunction with the ^{19}F NMR data, suggests the existence of solvent-separated ion pairs as found for N(PPh$_3$)$_2$ derivatives **6a** and **6b**. Interestingly though there is a noticeable change in the ^{133}Cs chemical shift over this temperature range from δ −26.9 (0) to −11.7 (−80 °C). In deuteriated toluene coupling between the Cs$^+$ and the *o*-fluorines was observed at all temperatures studied, 20 to −80 °C, indicating co-ordination of Cs$^+$. Owing to limited solubility of the complex this was not well resolved in the ^{19}F NMR spectra (Fig. 2) but $J_{\text{Cs–F}}$ values of 31.6 and 66.7 Hz were obtained at 20 and −80 °C respectively from the ^{133}Cs spectrum. The latter value reflects coupling of Cs$^+$ to one *o*-fluorine on each stereochemically rigid C$_6$F$_4$H and this gives rise to a well resolved quintet in the ^{133}Cs spectrum. At higher temperatures when C$_6$F$_5$ rotation ensues all eight *o*-fluorines couple with Cs$^+$ but with an average coupling constant which is half the low-temperature value. As with Cs[W(SC$_6$F$_5$)$_4$(η^5-C$_5$H$_5$)] and the thallium derivatives, intermediate behaviour was observed in CD$_2$Cl$_2$. Consequently the spectra are comparable to those of Cs[M(SC$_6$F$_5$)$_4$(η^5-C$_5$H$_5$)] (M = Mo or W)[4] and a similar explanation is therefore proposed, *i.e.* in C$_6$D$_5$CD$_3$ the Cs$^+$ cation co-ordinates with the organometallic anion at all temperatures between 20 and −80 °C. In CD$_2$Cl$_2$ co-ordination occurs at low temperatures but significant dynamic dissociation occurs at higher temperatures leading to loss of Cs–F coupling at room temperature. In acetone the ions appear to be well separated or at least undergo very fast exchange between free and co-ordinated states at all temperatures studied. As with the thallium derivatives the anion exhibits fluxional motion involving the SC$_6$F$_4$H-4 ligands in all solvents, presumably undergoing inversion and/or rotation at sulfur combined with rotation about the S–C$_6$F$_4$H-4 bond.

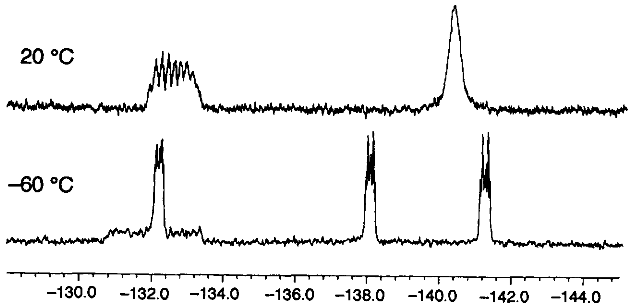


Fig. 2 The ^{19}F NMR spectra of Cs[W(SC$_6$F$_4$H-4)$_4$(η^5-C$_5$H$_5$)] in C$_6$D$_5$CD$_3$ at 20 and −60 °C

Dynamic ^{19}F NMR studies of the potassium and rubidium derivatives **4c** and **4d** were made in deuteriated toluene where co-ordination was more probable but, as with the SC$_6$F$_5$ derivatives,[4] the data obtained were less informative. These complexes exhibit fluxional behaviour at room temperature with both *o*- and *m*-fluorine resonances broadened significantly. At lower temperatures these split into two sets of well resolved peaks with no evidence for spin–spin interactions between the cation and the *o*-fluorines at −80 °C. This indicates that if co-ordination is occurring the lack of observable effects could be attributed to the relatively large quadrupole moments of K$^+$ and Rb$^+$ compared to Tl$^+$ and Cs$^+$ and this eliminates distinctive coupling to the fluorine nuclei. Alternatively, static co-ordination of the metal cations does not occur. It is of interest that Plenio and Burth[13] carried out studies of the complexation of metal ions Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Tl$^+$ with the fluorine-containing polydentate ligand FC$_6$H$_3$[CH$_2$-N(CH$_2$CO$_2$H)$_2$]-2,6. The observed shifts of the ^{19}F NMR resonance were attributed to fluorine co-ordination to the metal cations although no mention was made of Tl–F coupling.

The ^{19}F NMR spectrum of Na[W(SC$_6$F$_4$H-4)$_4$(η^5-C$_5$H$_5$)]·thf **5** was recorded in both CD$_2$Cl$_2$ and deuteriated toluene and at 20 °C shows similar features in both solvents, *viz.* two peaks one slightly broad the other very broad. At lower temperatures the latter separates out into two distinct peaks by −20 °C at which point the former is still a single broad resonance. However, in CD$_2$Cl$_2$ four distinct peaks due to two sets of inequivalent *ortho* and *meta* peaks are present at −40 °C indicating freezing out of a preferred conformation of the SC_6F_4H-4 groups. This occurs at *ca.* −70 °C in deuteriated toluene. However, no evidence was found in either solvent for sodium–fluorine interactions which might indicate ion pairing. The ^1H NMR spectrum contains, in addition to the η^5-C_5H_5 singlet and a SC_6F_4H-4 multiplet, two multiplets due to the thf of solvation. Integrated ratios are in accord with one molecule of thf as are the analytical data.

It is interesting to compare complex **5** with the polymeric sodium salt of $[Ti\{S(CH_2)_3S\}_2(\eta^5\text{-}C_5H_5)]^-$], which crystallises in two different forms.[14] The first, **7**, contains a sodium cation co-ordinated by a thf molecule and four sulfurs, two from one $[Ti\{S(CH_2)_3S\}_2(\eta^5\text{-}C_5H_5)]^-$ ion and two from another. The second is similar except that the sodium is co-ordinated by two thf molecules, two nearby sulfurs and two longer contacts to two other sulfurs. The two structures are somewhat similar to that found for $Tl[Mo(SC_6F_5)_2(CO)_2(\eta^5\text{-}C_5H_5)]$ in which the Tl^+ cation is co-ordinated by two sulfurs of one $[Mo(SC_6F_5)_2(CO)_2(\eta^5\text{-}C_5H_5)]$ anion, Tl–S *ca.* 300 pm, and makes two intermolecular contacts *ca.* 333 and 378 pm to two others of a second anion so as to produce a chain structure in the solid state.[1] However, as with $Tl[Mo(SC_6F_4H\text{-}4)_2(CO)_2(\eta^5\text{-}C_5H_5)]$ **3** reported here, and unlike **7**, clear NMR evidence was obtained for solvent-dependent ion pairing in solution. We note that Stephan and co-workers also reported some evidence for the formation of the anion $[Ti\{S(CH_2)_3S\}(SPh)_2(\eta^5\text{-}C_5H_5)]^-$ in solution but attempts to isolate this analogue of $[M(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]^-$ and $[M(SC_6F_4H\text{-}4)_4(\eta^5\text{-}C_5H_5)]^-$ (M = Mo or W) as the sodium or tetraalkylammonium salt failed. It is therefore conceivable that although we are unable to provide evidence for ion pairing in solution, the sodium ion in $Na[W(SC_6F_4H\text{-}4)_4(\eta^5\text{-}C_5H_5)]\cdot$thf is co-ordinated by both thf and the organometallic anion and in the solid state has the structure illustrated in Scheme 1. In a later publication Nadasdi and Stephan[15] reported the ability of bis(dithiolate)anions $[Ti\{S(CH_2)_3S\}_n(\eta^5\text{-}C_5H_5)]^-$ (n = 2 or 3) to co-ordinate to metals such as Cu and Rh. This contrasts with our earlier attempts to co-ordinate Group 11 metals to anions $[M(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]^-$ (M = Mo or W).[5] It therefore appears that although the titanium complexes reported by Stephan and co-workers exhibit some general similarities to the molybdenum and tungsten derivatives we have studied in recent years, significant differences in detailed behaviour exist.

Attempts were also made to prepare complexes containing a mixture of thiolate ligand types. In this and previous studies[1–3] we have demonstrated the ability of SC_6F_4X-4 (X = H or F) ligands successively to replace halide or carbonyl ligands, equations (1)–(5), and these reactions provide a basis for several

$$[MoCl(CO)_3(\eta^5\text{-}C_5H_5)] + Tl[SC_6F_4X\text{-}4] \longrightarrow [Mo(SC_6F_4X\text{-}4)(CO)_3(\eta^5\text{-}C_5H_5)] \quad (1)$$

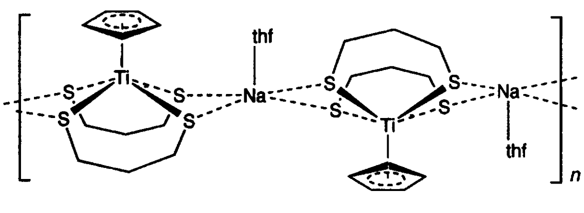
$$[MoCl(CO)_3(\eta^5\text{-}C_5H_5)] + 2\,Tl[SC_6F_4X\text{-}4] \longrightarrow Tl[Mo(SC_6F_4X\text{-}4)_2(CO)_2(\eta^5\text{-}C_5H_5)] \quad (2)$$

$$Tl[Mo(SC_6F_4X\text{-}4)_2(CO)_2(\eta^5\text{-}C_5H_5)] + 2\,(SC_6F_4X\text{-}4)_2 \longrightarrow [M(SC_6F_4X\text{-}4)_4(\eta^5\text{-}C_5H_5)] \quad (3)$$

$$[WX_3(CO)_2(\eta^5\text{-}C_5H_5)] + 3Tl[SC_6F_4X\text{-}4] \longrightarrow [W(SC_6F_4X\text{-}4)_3(CO)(\eta^5\text{-}C_5H_5)] \quad (4)$$

$$[W(SC_6F_4X\text{-}4)_3(CO)(\eta^5\text{-}C_5H_5)] + Tl[SC_6F_4X\text{-}4] \longrightarrow Tl[W(SC_6F_4X\text{-}4)_4(\eta^5\text{-}C_5H_5)] \quad (5)$$

synthetic strategies. Unfortunately, in all of the reactions attempted the products appeared to consist of a mixture of species according to NMR data. For example, the reaction of $[Mo(SC_6F_5)(CO)_3(\eta^5\text{-}C_5H_5)]$ with $Tl[SC_6F_4H\text{-}4]$ in diethyl ether gave a red crystalline solid which exhibited two ν(CO) modes in the IR spectrum at 1954 and 1872 cm^{-1}. This compares closely with 1955 and 1875 cm^{-1} for $Tl[Mo(SC_6F_5)_2(CO)_2(\eta^5\text{-}C_5H_5)]$ implying that the expected product $Tl[Mo(SC_6F_5)(SC_6F_4H\text{-}4)(CO)_2(\eta^5\text{-}C_5H_5)]$ has been obtained. However, the ^{19}NMR data suggest the presence of two species and all attempts to separate the mixture were unsuccessful. A similar situation occurred with the photolytic reaction of $Tl[Mo(SC_6F_5)_2(CO)_2(\eta^5\text{-}C_5H_5)]$ and $(SC_6F_4H\text{-}4)_2$ in an effort to prepare $[Mo(SC_6F_5)_2(SC_6F_4H\text{-}4)_2(\eta^5\text{-}C_5H_5)]$ and with the attempted preparation of $[W(SC_6F_5)_3(SC_6F_4H\text{-}4)(\eta^5\text{-}C_5H_5)]$ from the reaction of $[W(SC_6F_5)_3(CO)(\eta^5\text{-}C_5H_5)]$ with $Tl[SC_6F_4H\text{-}4]$. Similarly, the reaction of $[W(SC_6F_4H\text{-}4)_3(CO)(\eta^5\text{-}C_5H_5)]$ with $Tl[SC_6F_5]$ afforded a yellow powder which gave reasonable elemental analysis for the stoichiometry $[W(SC_6F_4H\text{-}4)_3(SC_6F_5)(\eta^5\text{-}C_5H_5)]$ but ^1H and ^{19}F NMR suggested a mixture. In all of these reactions it seems that although the expected product may be formed initially by halide or CO substitution additional thiolate-exchange reactions also occur readily leading to mixtures of products.



7

Conclusion

Previously we showed that thallium derivatives $Tl[Mo(SC_6F_5)_2(CO)_2(\eta^5\text{-}C_5H_5)]$ and $Tl[M(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) can readily be prepared from the reactions of appropriate molybdenum and tungsten precursors with $Tl[SC_6F_5]$. The results of the present study indicate that with significantly less electron-withdrawing groups on sulfur similar ionic species are not accessible by these routes. It did prove possible to isolate neutral tungsten(IV) derivatives $[W(SPh)_3(CO)(\eta^5\text{-}C_5H_5)]\cdot 0.25CH_2Cl_2$ and $[W(SC_6H_4Me\text{-}4)_3(CO)(\eta^5\text{-}C_5H_5)]$ which are the analogues of $[W(SC_6F_5)_3(CO)(\eta^5\text{-}C_5H_5)]$ structurally characterised previously. This illustrates that the tungsten(IV) oxidation state is accessible with arene thiolate ligands but the tetrathiolate anions could not be obtained by further reaction of these species with an excess of thallium thiolate. It is conceivable that these are unstable with respect to dimerisation or polymerisation to give sulfur-bridged species but we have no direct evidence for this. The chemistry of the SC_6F_4H-4 ligand is more akin to that of SC_6F_5 and both neutral and ionic molybdenum- and tungsten-(IV) complexes were readily isolated. As with $[W(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]^-$ it also proved possible to isolate both thallium and alkali-metal derivatives and demonstrate that ion pairing occurs readily with thallium and caesium derivatives in solution presumably as a result of co-ordination of the four thiolate sulfurs or fluorines.[4] This is of interest from a biological point of view since it has recently been reported that Tl^+ but not Cs^+ is incorporated into the reduced $[Fe_3S_4]^0$ and oxidised $[Fe_3S_4]^+$ clusters of *Pyrococcus furiosus* ferredoxin to give $[TlFe_3S_4]^+$ or $[TlFe_3S_4]^{2+}$.[6] This difference presumably reflects the difference in the propensity for ionic *versus* covalent interactions of the two ions. Since both Tl^+ and Cs^+ are both co-ordinated by organometallic ligands $[W(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]^-$ and $[W(SC_6F_4H\text{-}4)_4(\eta^5\text{-}C_5H_5)]^-$, the metal–sulfur interactions we have identified are presumably fairly ionic in nature. Alternatively co-ordination of $[W(SC_6F_4H\text{-}4)_4(\eta^5\text{-}C_5H_5)]^-$ to Cs^+ may involve a bonding interaction with four of the *o*-fluorines of the C_6F_4H-4 substituents as suggested previously for $Cs[W(SC_6F_4H\text{-}4)_4(\eta^5\text{-}C_5H_5)]$.[4] Some evidence for fluorine co-ordination to alkaline-earth-metal cations and Tl^+ has recently been reported.[13]

Experimental

All reactions and manipulations were carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. All solvents were thoroughly dried before use with sodium–benzophenone (toluene, diethyl ether, tetrahydrofuran and light petroleum) and phosphorus pentaoxide (dichloromethane). The light petroleum had a boiling range of 60–80 °C. The starting materials $[\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$,[16–18] $[\{W(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$,[17,18] $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$,[17,19] $[WX_3(CO)_2(\eta^5\text{-}C_5H_5)]$ (X = Cl or Br)[20] and $Tl[Mo(SC_6F_5)_2(CO)_2(\eta^5\text{-}C_5H_5)]$[1] were prepared by literature methods. The salts $M'[SC_6F_4H\text{-}4]$ (M′ = Na, K, Rb, Cs or Tl) were prepared as described previously[1,4] for the SC_6F_5 derivatives using $HSC_6F_4H\text{-}4$ instead of HSC_6F_5. Molybdenum and tungsten hexacarbonyls, benzenethiol, 2,3,5,6-tetrafluoro-, pentafluorobenzenethiol, thallium(I) acetate and bis(triphenylphosphoranediyl) ammonium chloride were obtained commercially (BDH, Aldrich, Ventron), and used as supplied.

Proton, ^{19}F, ^{31}P and ^{133}Cs NMR spectra were recorded on a Bruker WP 200 SY spectrometer at 200.13, 188.31, 80.32 and 25.25 MHz respectively using $SiMe_4$, CCl_3F, 85% aqueous H_3PO_4 and 0.1 mol dm^{-3} CsCl(aq) as references (δ 0.0), IR spectra in solution (CH_2Cl_2) on a Perkin-Elmer 1600 Fourier-transform spectrometer. Elemental analyses were carried out at the University of Manchester, Institute of Science and Technology.

Reactions

$[WBr_3(CO)_2(\eta^5\text{-}C_5H_5)]$. (*a*) *With* 3 Tl[SPh]. The complex $[WBr_3(CO)_2(\eta^5\text{-}C_5H_5)]$ (3.55 g, 6.53 mmol) and Tl[SPh] (6.14 g, 19.58 mmol) were stirred in dichloromethane (40 cm^3) for 1 d. The solution was filtered, centrifuged and concentrated *in vacuo*. Light petroleum was added and the solution cooled to −15 °C to yield green-brown crystals of $[W(SPh)_3(CO)(\eta^5\text{-}C_5H_5)]\cdot 0.25CH_2Cl_2$ **1a**, 1.84 g (45%) (Found: C, 46.3; H, 3.3; S, 14.7. $C_{24.25}H_{20.5}Cl_{0.5}OS_3W$ requires C, 46.6; H, 3.3; S, 15.4%). IR: ν(CO) 2015 cm^{-1}. ^1H NMR (CD_3COCD_3, 20 °C); δ 7.30–7.09 (m, 15 H, C_6H_5), 5.65 (s, 5 H, C_5H_5) and 5.62 (s, 0.5 H, CH_2Cl_2).

(*b*) *With* 3 $Tl[SC_6H_4Me\text{-}4]$. The complex $[WBr_3(CO)_2(\eta^5\text{-}C_5H_5)]$ (1.14 g, 1.3 mmol) and $Tl[SC_6H_4Me\text{-}4]$ (113 g, 3.9 mmol) were stirred in dichloromethane (50 cm^3) for 3 d. The dark brown solution was filtered, centrifuged and concentrated *in vacuo*. Light petroleum was added and the solution cooled to −15 °C affording dark brown crystals. These were recrystallised from dichloromethane–light petroleum to give $[W(SC_6H_4Me\text{-}4)_3(CO)(\eta^5\text{-}C_5H_5)]$ **1b**, 0.40 g (53%). Satisfactory analytical data were not obtained due to sample instability. IR (CH_2Cl_2): ν(CO) 2023 cm^{-1}. ^1H NMR (CD_2Cl_2, 30 °C): δ 7.10 (dd, 12 H, $3C_6H_4$), 5.45 (s, 5 H, C_5H_5) and 2.40 (s, 9 H, $3CH_3$)

$[WCl_3(CO)_2(\eta^5\text{-}C_5H_5)]$ with 3 $Tl[SC_6F_4H\text{-}4]$. The complex $[WCl_3(CO)_2(\eta^5\text{-}C_5H_5)]$ (2.23 g, 5.42 mmol) and $Tl[SC_6F_4H\text{-}4]$ (6.27 g, 16.26 mmol) were stirred in dichloromethane (40 cm^3) for 3d. The solution was filtered, centrifuged and concentrated *in vacuo*. Light petroleum was added and the solution cooled to −15 °C to yield orange-brown crystals of $[W(SC_6F_4H\text{-}4)_3(CO)(\eta^5\text{-}C_5H_5)]$ **1c**, 2.15 g (48%) (Found: C, 34.8; H, 0.9; S, 11.3. $C_{24}H_8F_{12}OS_3W$ requires C, 35.1; H, 1.0; S, 11.7%). IR: ν(CO) 2023 cm^{-1}. ^1H NMR (CD_2Cl_2, 20 °C): δ 7.00 (m, 3 H, $SC_6F_4H\text{-}4$) and 5.61 (s, 5 H, C_5H_5).

$[\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$ with $(SC_6F_4H\text{-}4)_2$. The complex $[\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$ (410 mg, 0.84 mmol) and $(SC_6F_4H\text{-}4)_2$ (400 mg, 1.45 mmol) were photolysed in toluene (60 cm^3) with a medium-pressure mercury lamp for 12 h. The solution was concentrated *in vacuo* and chromatographed on Florisil with 10% diethyl ether–light petroleum. The solution was concentrated *in vacuo* and cooled to −15 °C to afford orange-red crystals of $[Mo(SC_6F_4H\text{-}4)(CO)_3(\eta^5\text{-}C_5H_5)]$ **2** (437 mg, 61%) (Found: C, 39.2; H, 1.5; S, 7.4. $C_{14}H_6F_4MoO_3S$ requires C, 39.5; H, 1.4; S, 7.5%). IR: ν(CO) 2041 and 1956 cm^{-1}. NMR ($CDCl_3$, 20 °C): ^1H, δ 6.80 (m, 1 H, $SC_6F_4H\text{-}4$) and 5.62 (s, 5 H, C_5H_5); ^{19}F, δ −132.20 (m, 2 *o*-F) and −140.31 (m, 2 *m*-F)

$[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ with 2 $Tl[SC_6F_4H\text{-}4]$. The complex $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ (494 mg, 1.76 mmol) and $Tl[SC_6F_4H\text{-}4]$ (1.358 g, 3.52 mmol) were stirred in diethyl ether (40 cm^3) for 48 h. The solution was evaporated to dryness and extracted with light petroleum. The solution was concentrated *in vacuo* and chromatographed over Florisil with 10% diethyl ether–light petroleum. Concentration of the orange band and cooling to −15 °C afforded orange crystals of $[Mo(SC_6F_4H\text{-}4)(CO)_3(\eta^5\text{-}C_5H_5)]$ **2**, 247 mg (33%), identified by comparison with an authentic sample.

The residue from the petroleum extraction was recrystallised from dichloromethane–light petroleum and gave dark red crystals of the air-sensitive complex $Tl[Mo(SC_6F_4H\text{-}4)_2(CO)_2(\eta^5\text{-}C_5H_5)]$ **3** in two batches (total 126 mg, 9%) (Found: C, 29.1; H, 1.1; S, 8.7. $C_{19}H_7F_8MoO_2STl$ requires C, 29.1; H, 0.9; S, 8.2%). IR: ν(CO) 1953 and 1871 cm^{-1}. NMR (20 °C): ^1H ($CDCl_3$), δ 6.93 (m, 2 H, $SC_6F_4H\text{-}4$) and 5.70 (s, 5 H, C_5H_5); ^{19}F(CD_3COCD_3), δ −130.40 (br m, 4 *o*-F) and −140.50 (m, 4 *m*-F).

$Tl[Mo(SC_6F_4H\text{-}4)_2(CO)_2(\eta^5\text{-}C_5H_5)]$ 3 with $(SC_6F_4H\text{-}4)$. The complex $Tl[Mo(SC_6F_4H\text{-}4)_2(CO)_2(\eta^5\text{-}C_5H_5)]$ (188 mg, 0.24 mmol) and $(SC_6F_4H\text{-}4)_2$ (100 mg, 0.28 mmol) were photolysed in tetrahydrofuran (40 cm^3) with a medium-pressure mercury lamp for 12 h. The solution was evaporated to dryness and extracted into dichloromethane. This was then filtered, centrifuged and concentrated *in vacuo*. Light petroleum was added and the solution cooled to −15 °C to afford red microcrystals of $Tl[Mo(SC_6F_4H\text{-}4)_4(\eta^5\text{-}C_5H_5)]$ **4a**, 154 mg (59%) (Found: C, 31.7; H, 0.9; S, 11.4. $C_{29}H_9F_{16}MoS_4Tl$ requires C, 32.0; H, 0.8; S, 11.8%). NMR: ^1H ($CDCl_3$, 20 °C), δ 6.95 (m, 4 H, $SC_6F_4H\text{-}4$) and 5.60 [d, *J*(Tl–H) 4.1, 5 H, C_5H_5]; ^{19}F($CDCl_3$, 20 °C), δ −130.24 [br d, *J*(Tl–F) *ca.* 1700, 8 *o*-F] and −139.06 (m, 8 *m*-F); (CD_2Cl_2, −80 °C), δ −129.33 [br d, *J*(Tl–F) ≈ 3500 Hz, 4 *o*-F], −131.63 (br t, 4 *o*-F), −138.48 (m, 4 *m*-F) and −140.26 (m, 4 *m*-F).

$[WBr_3(CO)_2(\eta^5\text{-}C_5H_5)]$ with 5 $Tl[SC_6F_4H\text{-}4]$. The complex $[WBr_3(CO)_2(\eta^5\text{-}C_5H_5)]$ (520 mg, 0.95 mmol) and $Tl[SC_6F_4H\text{-}4]$ (1840 mg, 4.77 mmol) were stirred in dichloromethane (40 cm) for 7 d. The solution was filtered, centrifuged and the supernatant liquid removed and concentrated *in vacuo*. Light petroleum was added and the solution cooled to −15 °C to give $Tl[W(SC_6F_4H\text{-}4)_4(\eta^5\text{-}C_5H_5)]$ **4b** as a yellow powder, 219 mg (20%) (Found: C, 29.4; H, 0.7; S, 10.5. $C_{29}H_9F_{16}S_4TlW$ requires C, 29.6; H, 0.8; S, 10.9%). NMR (CD_2Cl_2, 20 °C): ^1H, δ 7.02 (m, 4 H, $SC_6F_4H\text{-}4$) and 5.53 [d, *J*(Tl–H) 2.8, 5 H, C_5H_5]; ^{19}F, δ −130.17 [br d, *J*(Tl–F) ≈ 1900 Hz, 8 *o*-F] and −139.84 (m, 8 *m*-F).

$[W(SC_6F_4H\text{-}4)_3(CO)(\eta^5\text{-}C_5H_5)]$. (*a*) *With* $Na[SC_6F_4H\text{-}4]$. The complex $[W(SC_6F_4H\text{-}4)_3(CO)(\eta^5\text{-}C_5H_5)]$ (0.3 g, 0.37 mmol) and $Na[SC_6F_4H\text{-}4]$ (0.047 g, 0.37 mmol) were stirred for 2 d in tetrahydrofuran (40 cm^3). The solution was evaporated to dryness, the residue extracted with dichloromethane (100 cm^3), centrifuged and the supernatant liquid removed and concentrated *in vacuo*. Addition of light petroleum and cooling to −15 °C gave a green crystalline solid $Na[W(SC_6F_4H\text{-}4)_4(\eta^5\text{-}C_5H_5)]\cdot thf$, **5**, 0.15 g (40%) (Found: C, 37.4; H, 1.7; S, 12.7). $C_{33}H_{17}F_{16}NaOS_4W$ requires C, 37.1; H, 1.6; S, 12.0%). NMR: ^1H (CD_2Cl_2, 20 °C), δ 1.93 (m, 4 H, thf); 3.83 (m, 4 H, thf); 5.35 (s, 5 H, C_5H_5) and 6.98 (m, 4 H, $4C_6F_4H$); ^{19}F (CD_2Cl_2, 20 °C), δ −137.62 (br, 8 *o*-F) and −140.28 (br, 8 *m*-F);

^{19}F(CD_2Cl_2, −80 °C), δ −134.05 (br, 4 *o*-F), −138.33 (m, 4 *o*-F), δ −139.80 (br, 4 *m*-F) and −140.77 (m, 4 *m*-F).

(*b*) *With* K[SC_6F_4H-4]. The complex [W(SC_6F_4H-4)$_3$(CO)(η^5-C_5H_5)] (0.3 g, 0.37 mmol) and K[SC_6F_4H-4] (0.081 g, 0.37 mmol) were stirred for 12 h in tetrahydrofuran (40 cm^3). The solution was evaporated to dryness and extracted with dichloromethane (200 cm^3), centrifuged and the supernatant liquid removed and concentrated *in vacuo*. Addition of light petroleum and cooling to −15 °C gave an impure (NMR) microcrystalline yellow solid. The product was recrystallised from diethyl ether–light petroleum affording K[W(SC_6F_4H-4)$_4$(η^5-C_5H_5)] **4c** as a yellow powder, 0.022 g (6%). NMR ($C_6D_5CD_3$): ^{1}H (20 °C), δ 5.25 (s, 5 H, C_5H_5) and 6.25 (m, 4 H, SC_6F_4H); ^{19}F (20 °C), δ −133.8 (br m, 8 *o*-F) and −140.6 (br m, 8 *m*-F); (−60 °C), δ −133.1 (m, 4 *o*-F), −137.8 (m, 4 *o*-F), −139.0 (m, 4 *m*-F) and −141.05 (m, 4 *m*-F).

With Rb[SC_6F_4H-4]. The complex [W(SC_6F_4H-4)$_3$(CO)(η^5-C_5H_5)] (0.3 g, 0.37 mmol) and Rb[SC_6F_4H-4] (0.098 g, 0.37 mmol) were stirred for 12 h in tetrahydrofuran (40 cm^3). The solution was evaporated to dryness and extracted into dichloromethane (200 cm^3), centrifuged and the supernatant liquid removed and concentrated *in vacuo*. Addition of light petroleum and cooling to −15 °C gave a microcrystalline yellow solid, Rb[W(SC_6F_4H-4)$_4$(η^5-C_5H_5)] **4d**, 0.11 (28%) (Found: C, 32.7; H, 0.9; S, 12.2. $C_{29}H_9F_{16}RbS_4W$ requires C, 32.9; H, 0.9, S, 12.1%). NMR: ^{1}H (CD_2Cl_2, 19 °C) δ 5.37 (s, 5 H, C_5H_5) and 6.98 (m, 4 H, C_6F_4H); ^{19}F($C_6D_5CD_3$, 19 °C), δ −134.65 (br, 8 *o*-F) and −139.9 (br, 8 *m*-F); (−20 °C), δ −132.75 (br, 4 *o*-F), −138.3 (br, 4 *m*-F) and −141.4 (br, 4 *m*-F).

(*d*) *With* Cs[SC_6F_4H-4]. The complex [W(SC_6F_4H-4)$_3$(CO)(η^5-C_5H_5)] (0.3 g, 0.37 mmol) and Cs[SC_6F_4H-4] (0.12 g, 0.37 mmol) were stirred for 12 h in tetrahydrofuran (40 cm^3). The solution was evaporated to dryness and extracted into dichloromethane (200 cm^3), centrifuged and the supernatant liquid removed and concentrated *in vacuo*. Addition of light petroleum and cooling to −15 °C gave a microcrystalline yellow solid Cs[W(SC_6F_4H-4)$_4$(η^5-C_5H_5)] **4e**, 0.20 g (51%) (Found: C, 31.4; H, 0.6; S, 11.9. $C_{29}H_9CsF_{16}S_4W$ requires C, 31.5; H, 0.8; S, 11.6%). NMR: ^{1}H (CD_2Cl_2, 20 °C), δ 5.38 (s, 5 H, C_5H_5) and 6.94 (m, 4 H, 4 C_6F_4H); ^{19}F ($C_6D_5CD_3$, 20 °C), δ −132.7 (m, 8 *o*-F) and −140.3 (br, 8 *m*-F); (−60 °C), δ −132.1 (br, 4 *o*-F), −132.3 (m, 4 *o*-F), −138.0 (m, 4 *m*-F) and −141.2 (m, 4 *m*-F); ^{133}Cs($C_6D_5CD_3$, 20 °C), δ −81.9 [qnt, *J*(Cs–F) 66.7 Hz]; (C_2D_6CO, 0 °C), δ −26.9 (s).

Tl[Mo(SC_6F_4H-4)$_4$(η^5-C_5H_5)] with [N(PPh_3)$_2$]Cl. The complex Tl[Mo(SC_6F_4H-4)$_4$(η^5-C_5H_5)] (80 mg, 0.073 mmol) and [N(PPh_3)$_2$]Cl (45 mg, 0.074 mmol) were stirred in dichloromethane (40 cm^3) for 1 h when a white precipitate formed. The solution was centrifuged and the supernatant liquid removed and concentrated *in vacuo*. Light petroleum was added and the solution cooled to −15 °C to give red-orange crystals of [N(PPh_3)$_2$][Mo(SC_6F_4H-4)$_4$(η^5-C_5H_5)] **6a**, 82 mg (78%) (Found: C, 54.8; H, 2.7; N, 1.2; S, 9.4. $C_{65}H_{39}F_{16}MoNP_2S_4$ requires C, 54.8; H, 2.8; N, 1.0; S, 9.0%). NMR ($CDCl_3$, 20 °C): ^{1}H, δ 7.63–7.37 (m, 30 H, C_6H_5), 6.69 (m, 4 H, SC_6F_4H-4) and 5.32 (s, 5 H, C_5H_5); ^{19}F, δ −130.71 (m, 8 *o*-F) and −142.58 (m, 8 *m*-F); ^{31}P-{^{1}H}, δ 22.07 (s, PPh_3).

Tl[W(SC_6F_4H-4)$_4$(η^5-C_5H_5)] with [N(PPh_3)$_2$]Cl. The complex Tl[W(SC_6F_4H-4)$_4$(η^5-C_5H_5)] (80 mg, 0.068 mmol) and [N(PPh_3)$_2$]Cl (40 mg, 0.070 mmol) reacted similarly to give yellow-green crystals of [N(PPh_3)$_2$][W(SC_6F_4H-4)$_4$(η^5-C_5H_5)] **6b**, 72 mg (70%) (Found: C, 51.3; H, 2.4; N, 1.1; S, 8.9. $C_{65}H_{39}F_{16}NP_2S_4W$ requires C, 51.6; H, 2.6; N, 0.9; S, 8.5%). NMR ($CDCl_3$, 20 °C): ^{1}H, δ 7.65–7.35 (m, 30 H, C_6H_5), 6.78–6.55 (m, 4 H, SC_6F_4H-4) and 5.27 (s, 5 H, C_5H_5); ^{19}F δ −131.11 (m, 8 *o*-F) and −142.58 (m, 8 *m*-F); ^{31}P-{^{1}H}, δ 22.07 (s, PPh_3).

Acknowledgements

We thank the EPSRC (N. J. S.) and the European Community (B. H.) for financial support.

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Received 20*th May* 1996; *Paper* 6/03488H