Reversible Co-ordination of Alkali Metals to Sulfur-based Organometallic Ligands $[M(SC_6F_5)_4(cp)]^-$ (M = Mo or W, cp = η^5-C_5H_5)

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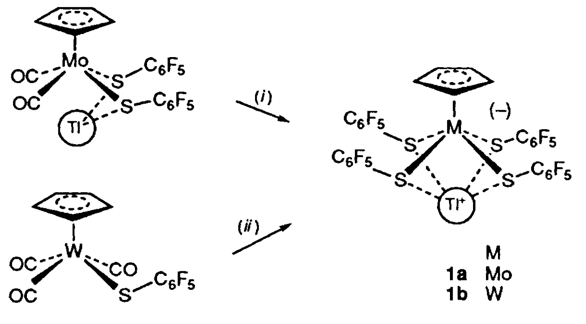
The photochemical reaction of $Tl[Mo(SC_6F_5)_2(CO)_2(cp)]$ (cp = η^5-C_5H_5) with $C_6F_5SSC_6F_5$ in tetrahydrofuran (thf) solution affords the tetrathiolate $Tl[Mo(SC_6F_5)_4(cp)]$. Similarly the photochemical reaction of $[W(SC_6F_5)(CO)_3(cp)]$ with 4 equivalents of $Tl(SC_6F_5)$ gave $Tl[W(SC_6F_5)_4(cp)]$ in low yield. Reactions of $[MI_3(CO)_2(cp)]$ (M = Mo or W) and $[W(SC_6F_5)_3(CO)(cp)]$ with $M'(SC_6F_5)$ in thf solution gave the ionic derivatives $Cs[Mo(SC_6F_5)_4(cp)]$, $M'[W(SC_6F_5)_4(cp)]$ (M' = Cs, Rb or K) and the solvated derivatives $[M'(thf)_n][W(SC_6F_5)_4(cp)]$ (M' = Li, *n* = 4; M' = Na, *n* = 1). Fluorine-19 NMR studies reveal fluxional behaviour involving the C_6F_5 groups in all the derivatives. Dynamic ^{133}Cs and ^{19}F NMR spectra of $Cs[M(SC_6F_5)_4(cp)]$ in addition show coupling between caesium and four of the *ortho*-fluorines of the SC_6F_5 groups, $J(Cs–F) \approx 58$ Hz, at low temperatures providing evidence for reversible co-ordination between Cs^+ and the organometallic anion.

Recently we reported the syntheses and dynamic NMR studies of the molybdenum[1] and tungsten[2] derivatives $Tl[M(SC_6F_5)_4(cp)]$ (M = Mo **1a** or W **1b**, cp = η^5-C_5H_5). X-Ray diffraction studies of **1a** and the $[N(PPh_3)_2]^+$ derivative $[N(PPh_3)_2][Mo(SC_6F_5)_4(cp)]$ revealed that the organometallic anion contains a cavity defined by the transition metal, four primary donor sites (sulfur) and four secondary sites (four *ortho*-fluorines of the C_6F_5 groups) which can encapsulate a Tl^+ ion. Variable-temperature ^{19}F NMR spectra of $Tl[M(SC_6F_5)_4(cp)]$ show solvent-dependent coupling between these four fluorines and $^{203/205}Tl$. At higher temperatures fluxional motion involving the SC_6F_5 groups is observed and this is accompanied in some solvents by deco-ordination of Tl^+ which leads to loss of coupling. The illustration that organometallic anions of this type could reversibly co-ordinate to a metal cation has wider implications in the fields of metal-ion sensors and sequestration reagents. It was therefore of interest to investigate the co-ordination capabilities of $[M(SC_6F_5)_4(cp)]^-$ and we decided to attempt the synthesis of related species containing counter ions other than thallium. The results of these studies, some of which have been reported previously as a communication,[3] are reported herein.



Scheme 1 (*i*) $C_6F_5SSC_6F_5$, *hν*; (*ii*) $4Tl(SC_6F_5)$, thf

Results and Discussion

Previously we reported that the thallium derivative $Tl[Mo(SC_6F_5)_4(cp)]$ **1a** could be obtained by reaction of $[MoCl(CO)_3(cp)]$ with >4 equivalents of $Tl(SC_6F_5)$ in tetrahydrofuran (thf), a reaction which proceeds *via* the Mo^{II} intermediate $Tl[Mo(SC_6F_5)_2(CO)_2(cp)]$.[1] However, the tungsten complex $Tl[W(SC_6F_5)_4(cp)]$ **1b** required a tungsten(IV) precursor such as $[WCl_3(CO)_2(cp)]$ and this reaction proceeds *via* the neutral monocarbonyl $[W(SC_6F_5)_3(CO)(cp)]$.[2] It was of interest to extend the available routes to tetrathiolate anions $[M(SC_6F_5)_4(cp)]^-$ and consequently the synthetic utility of carbonyl-containing intermediates was explored. It was subsequently found that the photochemical reaction of $Tl[Mo(SC_6F_5)_2(CO)_2(cp)]$ with $C_6F_5SSC_6F_5$ in thf solution affords the tetrathiolate **1a** in 56% yield (Scheme 1). The photochemical reaction of $[W(SC_6F_5)(CO)_3(cp)]$ with 4 equivalents of $Tl(SC_6F_5)$ similarly gave very small quantities (3% yield) of the tungsten complex $Tl[W(SC_6F_5)_4(cp)]$ **1b** (Scheme 1). Both of these reactions presumably proceed *via* photoejection of a carbonyl ligand thus allowing attack by the SC_6F_5-containing reagents. Initially we assumed that our inability to obtain **1b** from the reaction of $[W(SC_6F_5)(CO)_3(cp)]$ with $Tl(SC_6F_5)$ reflected the lack of reactivity of tungsten towards oxidation to W^{IV} but it now appears that the greater stability of tungsten tricarbonyl thiolates such as $[W(SC_6F_5)(CO)_3(cp)]$ towards CO loss[4] may be responsible.

Attention was then devoted to the synthesis of metal derivatives of the organometallic anions with cations other than thallium. Following our previous observation that the thallium ion in $Tl[Mo(SC_6F_5)_4(cp)]$ **1a** could readily be replaced by non-co-ordinating ions such as $[N(PPh_3)_2]^+$, $[NMe_4]^+$ and $[NBu^n{}_4]^+$ [2] it was anticipated that such species might afford a route to new metal derivatives by simple cation-exchange reactions. However, reactions of $Tl[Mo(SC_6F_5)_4(cp)]$ **1a** and $[NBu_4][Mo(SC_6F_5)_4(cp)]$ with a large excess of potassium iodide in acetone (a solvent which promotes thallium dissociation[1,2]) did not produce the desired potassium derivative. Analysis of the reaction mixture by NMR spectroscopy showed several C_6F_5-containing species, the spectra of which were of insufficient quality to allow deductions concerning the nature of the components produced and work-up gave a mixture of at least two compounds which could not be separated. An alternative method was then used involving a column of strongly acidic, sulfonated, cation-exchange resin in the Na^+ form. An acetone solution of $[NBu^n_4][Mo(SC_6F_5)_4(cp)]$ was continually passed through a column of the resin several times, but NMR analysis of the eluent revealed the presence of the starting material only.

In subsequent attempts to synthesise the Mo–Rb, Mo–Li, Mo–K and W–K tetrathiolates one of the original methods employed for the synthesis of the thallium derivatives **1** was utilised. Thus reactions of $[MoI_3(CO)_2(cp)]$ with $Rb(SC_6F_5)$ or $Li(SC_6F_5)$, $[MoCl_2(C_3H_5)(CO)(cp)]$ (C_3H_5 = allyl) with $K(SC_6F_5)$, and $[WI_3(CO)_2(cp)]$ with $K(SC_6F_5)$ using 1:5 molar ratios of the reactants were carried out. Considerable amounts of oily products and/or unidentified powders were produced but the desired pure compounds were not isolated and NMR studies of the reaction mixtures revealed that several different products were formed. However, the reactions of $[MI_3(CO)_2(cp)]$ (M = Mo or W) with $Cs(SC_6F_5)$ in thf at room temperature (see Scheme 2) afforded low yields of red (M = Mo) and yellow (M = W) microcrystalline products $Cs[Mo(SC_6F_5)_4(cp)]$ **3a** and $Cs[W(SC_6F_5)_4(cp)]$ **3d** after recrystallisation from dichloromethane–light petroleum at −15 °C.

An alternative and more successful route to the tungsten derivatives $M'[W(SC_6F_5)_4(cp)]$ was subsequently developed following an improved synthesis of the previously reported[2] monocarbonyl $[W(SC_6F_5)_3(CO)(cp)]$ **2**. In earlier studies the reaction between $[WBr_3(CO)_2(cp)]$ and a large excess of $Tl(SC_6F_5)$ in CH_2Cl_2 at 20 °C afforded $Tl[W(SC_6F_5)_4(cp)]$ **1b** as the major product (33%) and **2** as the minor product (3%).[2] This suggested that the tetrathiolate is formed *via* the carbonyl derivative **2** [equations (1) and (2)] with the final step in the

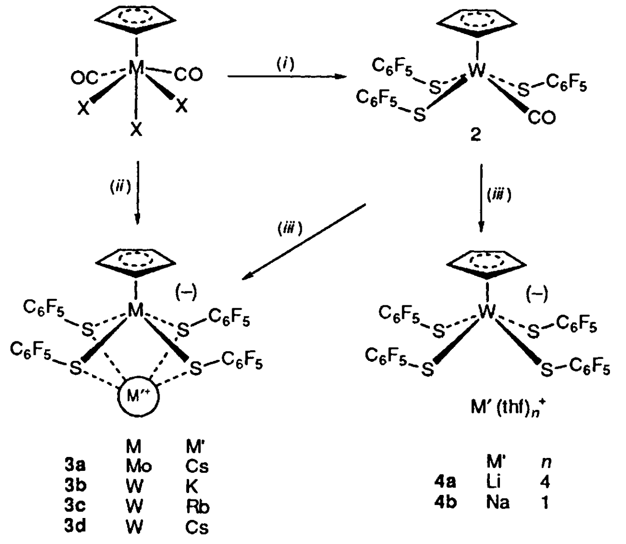
$$[WBr_3(CO)_2(cp)] + 3Tl(SC_6F_5) \longrightarrow [W(SC_6F_5)_3(CO)(cp)]\ \mathbf{2} \qquad (1)$$

$$\mathbf{2} + Tl(SC_6F_5) \longrightarrow Tl[W(SC_6F_5)_4(cp)]\ \mathbf{1b} \qquad (2)$$

reaction involving nucleophilic substitution of CO by $SC_6F_5^-$.

The reaction in equation (1) was repeated using 3 molar equivalents of $Tl(SC_6F_5)$ and **2** was obtained in 60% yield. However, the reaction sequence depicted in equations (1) and (2) is clearly an oversimplification since IR monitoring revealed that after a few hours the two characteristic CO stretching bands of $[WBr_3(CO)_2(cp)]$ are replaced by a broad band around 1942 cm^{-1} as well as the monocarbonyl band of **2** at 2023 cm^{-1}. The identity of the species responsible for the band at 1942 cm^{-1} has not been established. In a separate reaction 1 molar equivalent of $Tl(SC_6F_5)$ was added to **2** and this gave **1b** in essentially quantitative yield, confirming our original suggestion that **2** is the precursor to **1b**. Attempts were also made to obtain the analogous monocarbonyl molybdenum derivative $[Mo(SC_6F_5)_3(CO)(cp)]$ by a similar methodology. Unfortunately, although the IR spectra of the reaction mixture indicated the presence of such a species during reaction, it could not be isolated.

Reactions of $[W(SC_6F_5)_3(CO)(cp)]$ **2** with $M'(SC_6F_5)$ (see Scheme 2) in thf at room temperature afforded the yellow, microcrystalline products $M'[W(SC_6F_5)_4(cp)]$ (M′ = K **3b**, Rb **3c** or Cs **3d**) in 10–40% yield, after recrystallisation from dichloromethane–light petroleum or diethyl ether–light petroleum at −15 °C. In the case of the rubidium complex the crystals obtained from diethyl ether retained ether of crystallisation according to ^1H NMR spectroscopy but the crystals effloresced readily and the sample used for elemental analysis was obtained ether free after several hours under vacuum. In contrast reactions of $Li(SC_6F_5)$ and $Na(SC_6F_5)$ produced more stable thf-solvated products $[M'(thf)_n][W(SC_6F_5)_4(cp)]$ [M′ = Li, *n* = 4 **4a** (22%); M′ = Na, *n* = 1 **4b** (63%)] which, in the case of M′ = Na, could be converted to the thf-free species on repeated recrystallisation from dichloromethane. Solvation is confirmed by the ^1H NMR spectra of the sodium and lithium complexes which showed additional distinctive resonances corresponding to 1 mole of thf and 4 moles of thf, respectively. The 'hardness' of these two relatively small cations is presumably responsible for solvation by the oxygen donor thf. Elemental analysis is consistent with the formulae proposed for **3b**, **3c**, **3d** and **4b**. Crystals of **4a** were not submitted for elemental analyses as they appeared to be efflorescent; however, ^1H, ^7Li and ^{19}F NMR data for this compound were consistent with the formulation $[Li(thf)_4][W(SC_6F_5)_4(cp)]$.



Scheme 2 (*i*) $3Tl(SC_6F_5)$, thf, X = Cl; (*ii*) $5M'(SC_6F_5)$, thf, X = I; (*iii*) $M'(SC_6F_5)$, thf

The spectroscopic properties of the alkali-metal complexes are, in general, fairly similar to those of the previously reported thallium derivatives **1a** and **1b**. However, detailed differences are observed, particularly in the dynamic NMR spectra. The ^{133}Cs and ^{19}F NMR spectra of the caesium derivatives $Cs[M(SC_6F_5)_4(cp)]$ (M = Mo **3a** or W **3d**) were studied in detail. In order to assess the co-ordination capabilities of the anion with caesium the spectra were recorded in three solvents, $CD_3C_6D_5$, CD_2Cl_2 and $(CD_3)_2CO$, over the temperature range *ca.* 40 to −80 °C, and these illustrate three distinct phenomena: (*a*) reversible co-ordination of $[M(SC_6F_5)_4(cp)]^-$ to Cs^+, (*b*) fluxional motion involving the SC_6F_5 ligands, and (*c*) well resolved spin–spin coupling between ^{133}Cs and ^{19}F. Thus, at −20 °C and above in $CD_3C_6D_5$ the ^{133}Cs NMR spectrum of $Cs[Mo(SC_6F_5)_4(cp)]$ **3a** consists of a seven-line multiplet near δ −80. If we assume that one of the two outer lines of the expected nonet are lost in the noise this suggests that the Cs^+ is co-ordinated by the thiolate anion and is coupled to eight equivalent *ortho*-fluorines, *J*(Cs–F) = 29.7 Hz [Fig. 1(*a*)]. At this temperature the *ortho*-fluorines on each C_6F_5 group are clearly undergoing exchange presumably *via* rotation about the S–C_6F_5 bond rendering all of the eight *ortho*-fluorines equivalent. As the temperature is reduced the multiplet broadens, ultimately to give a quintet at −60 °C due to coupling to four equivalent *ortho*-fluorines, *J*(Cs–F) = 57.8 Hz [Fig. 1(*b*)]. These data indicate that the SC_6F_5 groups now adopt a fixed orientation at low temperature, as found in the solid state for $Tl[Mo(SC_6F_5)_4(cp)]$.[1] However, we emphasize that rotation/inversion of SC_6F_5 units, which interchanges each set of *ortho*- and *meta*-fluorines, clearly occurs without dissociation of Cs^+ in this solvent. Corresponding changes in the ^{19}F NMR spectrum are observed over the temperature range 40 to −80 °C. At 40 °C one set of *ortho*-, *meta*- and *para*-fluorine resonances is present; coupling to $^{133}Cs^+$ ($I = \frac{7}{2}$, 100% abundant) as well as to other fluorine atoms (principally one of the *meta*-fluorines) results in a complex multiplet for the *ortho*-

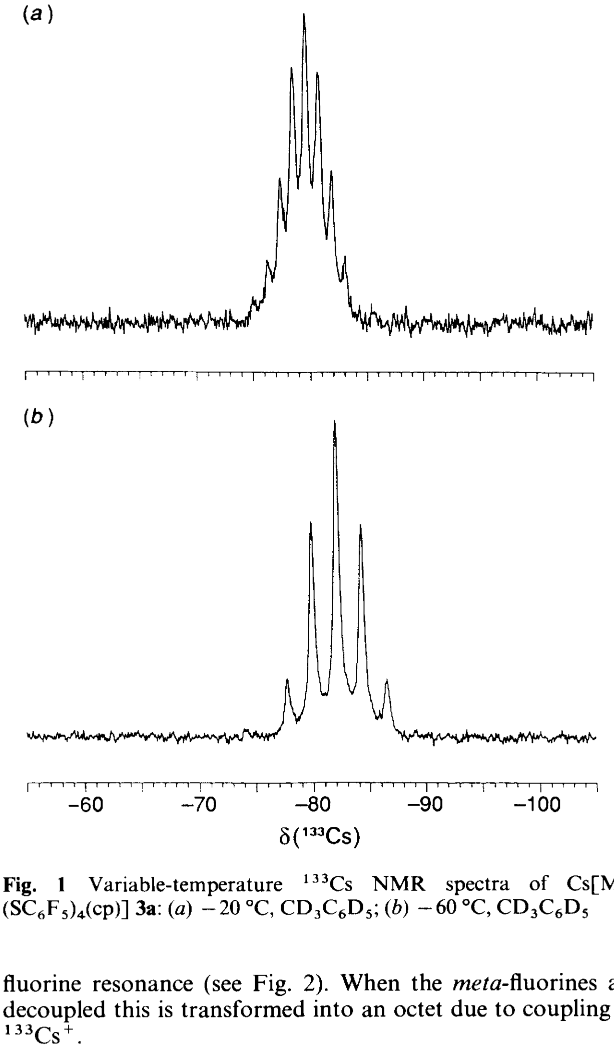


Fig. 1 Variable-temperature ^{133}Cs NMR spectra of Cs[Mo(SC_6F_5)$_4$(cp)] **3a**: (*a*) −20 °C, $CD_3C_6D_5$; (*b*) −60 °C, $CD_3C_6D_5$

fluorine resonance (see Fig. 2). When the *meta*-fluorines are decoupled this is transformed into an octet due to coupling to $^{133}Cs^+$.

At lower temperatures each *ortho* and *meta* resonance broadens and splits into two multiplets consistent with the adoption of a preferred orientation of the C_6F_5 groups with all fluorines on each equivalent ring inequivalent. Only one of the *ortho*-fluorine resonances shows coupling to caesium, as expected, but the coupling is not well resolved. In CD_2Cl_2 this coupling is clearly resolved at low temperatures but in this solvent evidence is also found for Cs^+ dissociation at higher temperatures.

At 30 °C in CD_2Cl_2 the ^{133}Cs NMR spectrum of **3a** consists of a singlet, δ −15.1, consistent either with non-interaction between Cs^+ and $[Mo(SC_6F_5)_4(cp)]^-$ ions or a fast exchange process involving these two species. As the temperature is reduced the singlet broadens and ultimately gives a quintet at −60 °C due to coupling to four equivalent *ortho*-fluorines, J(Cs–F) = 57.6 Hz, as above indicating co-ordination of the anion to Cs^+ (Fig. 3). In the ^{19}F NMR spectrum at room temperature no coupling to ^{133}Cs is observed and only one set of broad *ortho*-, *meta*- and *para*-fluorine resonances is present. At lower temperatures each *ortho* and *meta* resonance broadens and splits into two multiplets consistent with the adoption of a preferred orientation of the C_6F_5 groups. One of the two *ortho*-fluorine resonances only shows coupling with a *meta*- and a *para*-fluorine resulting in a doublet of doublets. However, the other is further split into eight equal intensity lines (*i.e.*, eight doublets of doublets) with well resolved coupling to ^{133}Cs, J(Cs–F) = 58.6 Hz (see Fig. 4). Since the larger of the J(F–F) values is approximately half that of J(Cs–F) the overall appearance is that of 16 doublets.

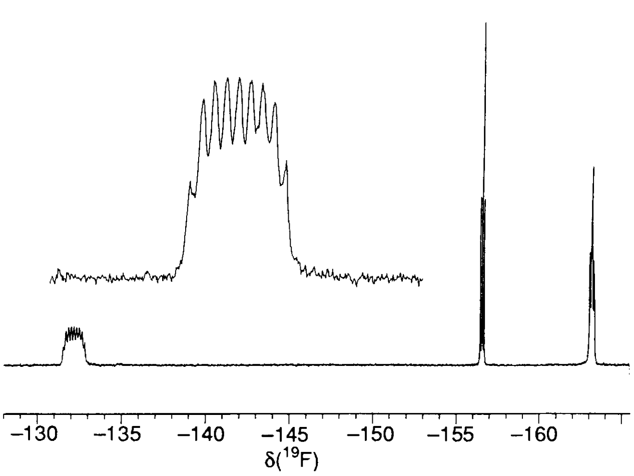


Fig. 2 Fluorine-19 NMR spectrum (non-decoupled) of Cs[Mo(SC_6F_5)$_4$(cp)] **3a** (−60 °C, $CD_3C_6D_5$) with expansion of the C_6F_5 *ortho*-fluorine resonances

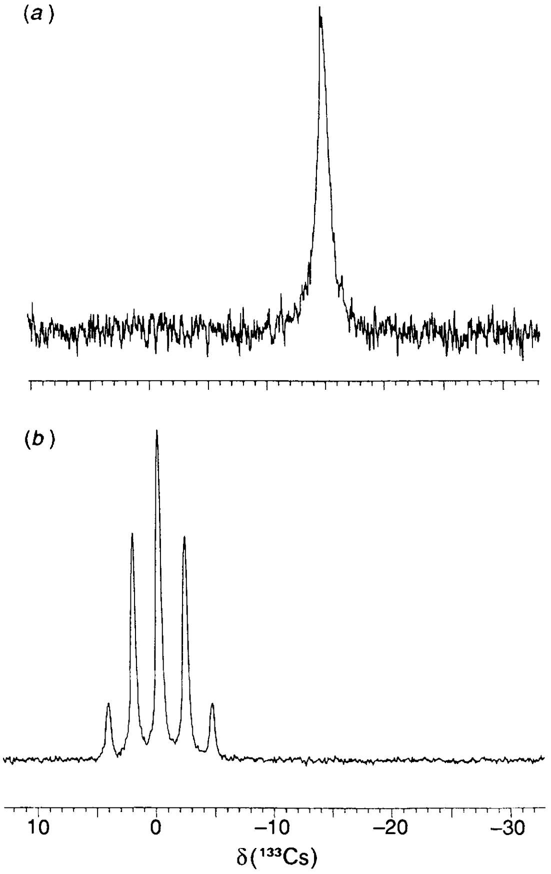


Fig. 3 Variable-temperature ^{133}Cs NMR spectra of Cs[Mo(SC_6F_5)$_4$(cp)] **3a**: (*a*) 20 °C, CD_2Cl_2; (*b*) −60 °C, CD_2Cl_2

In deuteriated acetone at room temperature three well resolved multiplets due to freely rotating C_6F_5 groups are observed in the ^{19}F NMR spectrum with no sign of Cs–F coupling. At lower temperatures the *ortho* and *meta* signals broaden and each splits into two multiplets indicating adoption of a preferred orientation at *ca.* −80 °C. However, in contrast with the other solvents no evidence for interaction with the Cs^+ counter ion was observed at low temperatures.

Variable-temperature ^{19}F NMR studies of the related tungsten derivative Cs[W(SC_6F_5)$_4$(cp)] **3d** in deuteriated toluene and dichloromethane produced broadly similar results except that coupling between the *ortho* fluorines and the guest caesium ion was less well resolved.

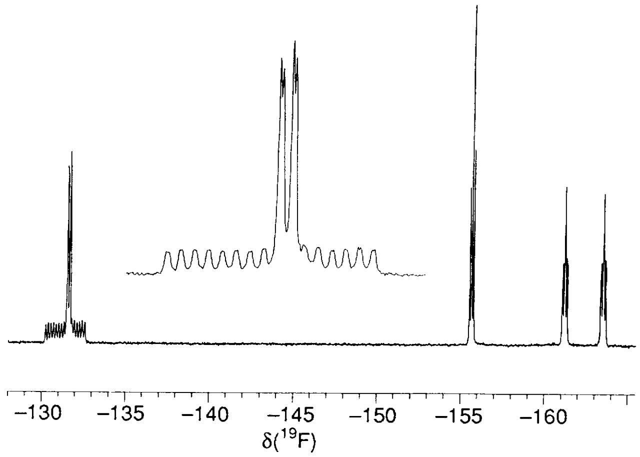


Fig. 4 Fluorine-19 NMR spectrum of Cs[Mo(SC$_6$F$_5$)$_4$(cp)] **3a** (−60 °C, CD$_2$Cl$_2$) with expansion of the C$_6$F$_5$ *ortho*-fluorine resonances

To summarise it appears that in CD$_3$C$_6$D$_5$ the cation is principally located in the cavity of the anion at all temperatures investigated, *i.e.* 40 °C and below. As a result only a small change in the chemical shift of the Cs$^+$ ion in the ^{133}Cs NMR spectrum is observed between room temperature and −60 °C, *ca.* 3 ppm. The distinct coupling between caesium and fluorine which provides evidence for this conclusion is the first reported example of spin–spin interactions between these nuclei. In CD$_2$Cl$_2$ ion association is observed at low temperature but dissociation occurs at higher temperatures and a much larger change in shift is observed, *ca.* 15 ppm, obviously reflecting the different environments of Cs$^+$ in this solvent at the two temperatures. 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. This parallels exactly the situation reported earlier for the thallium derivatives **1a** and **1b**.

Dynamic NMR studies of the potassium and rubidium derivatives **3b** and **3c** were less informative. These complexes exhibit fluxional behaviour at room temperature with both *ortho*- and *meta*-fluorine resonances broadened significantly in CD$_2$Cl$_2$. At lower temperatures these split into two sets of well resolved peaks with no evidence for spin–spin interactions between the cation and the *ortho*-fluorines even at −80 °C. If co-ordination is occurring the lack of observable effects could be attributed to the relatively large quadrupole moments of these nuclei compared to Tl$^+$ and Cs$^+$ which eliminates distinctive coupling to the fluorine nuclei. Alternatively, co-ordination of these ions does not occur. The ^{19}F NMR spectrum of the rubidium compound **3c** was also recorded in deuteriated toluene and essentially similar results were obtained down to −60 °C. Below this the lower frequency *ortho* peak showed some broadening, and by −80 °C was half the peak height of its neighbour. This may indicate a proximity effect with a neighbouring Rb$^+$ but the evidence is not conclusive. In an attempt to find evidence for cation co-ordination approximate energy barriers $\Delta G^\ddagger$ for C$_6$F$_5$ fluxional motion were calculated from coalescence temperatures of the *meta*- and in some cases, the *ortho*-fluorine peaks.

Barriers ($\Delta G^\ddagger$) to rotation/inversion for C$_6$F$_5$ rings for each complex in CD$_2$Cl$_2$ are: K[W(SC$_6$F$_5$)$_4$(cp)] **3b** ($\Delta G^\ddagger_{276}$ = 51.5 ± 0.5 kJ mol^{-1}), Rb[W(SC$_6$F$_5$)$_4$(cp)] **3c** ($\Delta G^\ddagger_{278}$ = 52.1 ± 0.5 kJ mol^{-1}) and Cs[W(SC$_6$F$_5$)$_4$(cp)] **3d** ($\Delta G^\ddagger_{272}$ = 50.9 ± 0.5 kJ mol^{-1}). These values compare with a $\Delta G^\ddagger_{226}$ value of *ca.* 41.0 ± 0.5 kJ mol^{-1} for the non-co-ordinated anion in [N(PPh$_3$)$_2$][Mo(SC$_6$F$_5$)$_4$(cp)] and $\Delta G^\ddagger_{229}$ = 43.4 ± 0.5 kJ mol^{-1} for [N(PPh$_3$)$_2$][W(SC$_6$F$_5$)$_4$(cp)].[5] However, these larger barriers do not necessarily provide evidence for co-ordination of the cation since the Tl$^+$ complex **1b**, where evidence for co-ordination is unambiguous, has a relatively small value ($\Delta G^\ddagger_{248}$ = 46.7 ± 0.8 kJ mol^{-1}). A similar value was obtained for the sodium compound [Na(thf)][W(SC$_6$F$_5$)$_4$(cp)] **4b** ($\Delta G^\ddagger_{255}$ = 46.6 ± 0.3 kJ mol^{-1}). The ^{23}Na NMR spectrum of this compound was also recorded and at 19 °C shows a broad single resonance at δ −9.36. At −60 °C there is a considerable shift to δ 27.17 which might suggest a change of environment in which the Na$^+$ ion co-ordinates to the anion. No spin–spin coupling could be observed which is to be expected in view of the large nuclear quadrupole moment of ^{23}Na.

Interestingly, the ^{19}F NMR spectrum of the lithium derivative **4a** in CD$_2$Cl$_2$ at 20 °C contains only one set of well resolved *ortho*-, *meta*- and *para*-fluorine resonances which is indicative of a species containing a non-co-ordinated cation presumably [Li(thf)$_4$]$^+$. This is supported by the low coalescence temperatures of 223 ± 5 K for both the *ortho*- and *meta*-fluorine resonances which correspond to a barrier to rotation for C$_6$F$_5$ rings of 41.3 ± 0.8 kJ mol^{-1}. This barrier is even lower than that of [N(PPh$_3$)$_2$][W(SC$_6$F$_5$)$_4$(cp)]. Attempts were made to desolvate **4a** in order to facilitate co-ordination of Li$^+$. This involved dissolving the solvated crystals in diethyl ether followed by evaporating the resulting solution to dryness. This was repeated several times with diethyl ether and finally with dichloromethane. Although the ^{1}H NMR spectrum of the yellow powder obtained showed the absence of thf, and a single sharp peak was obtained in the ^{7}Li NMR at δ 0.04 at −60 °C in CD$_2$Cl$_2$, the ^{19}F NMR indicated the presence of more than one species and the results of this experiment were inconclusive. Desolvation was also attempted by heating the compound under vacuum for several days at 50 °C. This, according to ^{1}H NMR data, was successful in removing the thf solvate from the crystal, but again the ^{19}F NMR spectrum indicated that several species were present in solution.

Interestingly, we note that variable-temperature ^{133}Cs NMR studies of Cs complexes with various cryptands suggest that two types of complex can exist in solution. In one form the Cs$^+$ ion is completely encapsulated by the cryptand, whilst in the other the metal ion is only partially enclosed within the ligand cavity.[6] The caesium and thallium complexes studied herein and earlier can, to some extent, be compared with the latter type of complex in that the guest metal Cs$^+$ or Tl$^+$ is only partially enclosed by the [M(SC$_6$F$_5$)$_4$(cp)]$^-$ ligand. We note that evidence was also found for partial solvation of the caesium ion in the partially enclosed cryptand complexes. It is therefore not surprising that the ^{133}Cs and ^{19}F NMR spectra of the thallium and caesium complexes are solvent dependent since the more polar solvents such as acetone can readily enter the co-ordination sphere of the partially exposed metal and thus facilitate deco-ordination from the [M(SC$_6$F$_5$)$_4$(cp)]$^-$ ligand.

Conclusion

The use of transition-metal complexes containing terminal thiolate ligands to co-ordinate other transition metals is well established[7] but co-ordination to alkali metals is, to our knowledge, unknown. As described earlier the thallium in Tl[Mo(SC$_6$F$_5$)$_4$(cp)] **1a** is co-ordinated primarily *via* the sulfurs, the interaction with four *ortho*-fluorines being essentially non-bonding. In contrast, the related Ru–SC$_6$F$_5$ chelate ring in [Ru(SC$_6$F$_4$F-2)(SC$_6$F$_5$)$_2$(PMe$_2$Ph)$_2$] contains a well defined Ru–F bond, Ru–F 2.489 Å.[8] It is therefore conceivable that in the metal derivatives described herein the alkali-metal ion may prefer co-ordination to the *ortho*-fluorine atoms as hard donors rather than the softer sulfur atoms of the SC$_6$F$_5$ groups. This question is not fully resolved by the NMR data which do not directly distinguish between the sulfur co-ordinated structure with secondary weak interactions to fluorine, as in Fig. 5, and the alternative fluorine co-ordinated form of Fig. 6. However, we note that fluxional behaviour which exchanges the C$_6$F$_5$ *ortho*-fluorines, presumably *via* rotation of the C_6F_5 group about the C–S bond, can occur without dissociation of the $[M(SC_6F_5)_4(cp)]^-$ ligand from the co-ordination sphere of the caesium ion in **3a** and **3d**. This is more consistent with the sulfur co-ordinated form illustrated in Fig. 5 since C_6F_5 rotation would result in fission of the Cs–F bond in the fluorine-bonded structure and thus facilitate dissociation.

It may be significant that fluorinated aromatic macrocycles in spherand ligands with complementary cavities for respective alkali-metal ions do not bind either Cs^+ or Li^+ [9] which also suggests that co-ordination by aromatic fluorine atoms is unlikely. However, the spherand ligands, unlike $[M(SC_6F_5)_4(cp)]^-$ are not negatively charged and this clearly affects their ability to co-ordinate to a cation. In this regard we note that co-ordination of lithium by fluorine has been observed in lithium organo(fluorosilyl)amides.*[,10]

Interestingly, reversible co-ordination of thallium(I) by an iron sulfur [3Fe–4S] cluster in 7Fe ferredoxin III has been reported recently and it was noted that this species was able to discriminate very effectively in favour of Tl^+ against K^+ and Rb^+.[11] On this basis binding was suggested to occur at the sulfurs of the tri-μ-sulfido face since these comprise the only polarizable ligand group on the protein. Co-ordination of Tl^+ by the crown thioether 1,4,7-trithiacyclononane ($[9]aneS_3$) has also been reported in the complex $[Tl([9]aneS_3)]PF_6$ and X-ray diffraction studies have shown that the trithia ligand is bound facially *via* the three sulfurs to the Tl^+ with a secondary Tl–S contact with a neighbouring $[Tl([9]aneS_3)]^+$ unit.[12] Significantly further secondary interactions with fluorines of three different PF_6^- units were also found, resulting in overall eight-co-ordination at thallium. This is reminiscent of the situation in $Tl[Mo(SC_6F_5)_4(cp)]$ **1a** where four sulfurs and four fluorines surround the Tl^+ ion. In contrast alkali metals prefer to co-ordinate with oxygen-based crown ethers[13] although co-ordination with sulfur donors and other soft bases is also known.[14] Whatever the mode of co-ordination it is clear that the organometallic ions $[Mo(SC_6F_5)_4(cp)]^-$ and $[W(SC_6F_5)_4(cp)]^-$ do not appear to exhibit significant discrimination in their ability to co-ordinate Tl^+ relative to alkali-metal ions. This and the fact that dissociation occurs readily in solution suggests that there is not much covalent electron-pair bonding between the metal ions and $[M(SC_6F_5)_4(cp)]^-$, *i.e.* the bonding interaction may be little more than that of an ion pair. We note that ion pairing between alkali-metal salts of metal carbonyl anions is well known[15] but the M–CO–cation interaction appears to be much less directional and somewhat weaker than the bonding reported herein.

Experimental

All reactions and manipulations were carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried thoroughly before use with sodium–benzophenone [toluene, diethyl ether, thf and light petroleum ether (b.p. range 60–80 °C)] and phosphorus pentaoxide (dichloromethane). Starting materials $Tl[Mo(SC_6F_5)_2(CO)_2(cp)]$,[1] $[NBu^n_4][Mo(SC_6F_5)_4(cp)]$,[2] $[MoI_3(CO)_2(cp)]$,[16] $[WI_3(CO)_2(cp)]$,[16] $Tl(SC_6F_5)$,[1] $C_6F_5SSC_6F_5$[17] and $Cs(SC_6F_5)$[18] were prepared by literature methods. Alkali-metal thiolates $Li(SC_6F_5)$, $Na(SC_6F_5)$, $K(SC_6F_5)$ and $Rb(SC_6F_5)$ were prepared by adaptation of the method originally reported for the caesium compound. The compounds $[Mo(CO)_6]$, $[W(CO)_6]$, pentafluorobenzenethiol, thallium(I) acetate, sodium, potassium, rubidium and caesium hydroxide and $[N(PPh_3)_2]Cl$ were obtained commercially (BDH, Aldrich, Ventron), and used as supplied. Proton, ^7Li, ^{19}F, ^{23}Na, ^{31}P, ^{87}Rb and ^{133}Cs NMR spectra were recorded on a Bruker WP 200 SY instrument at 200.13, 77.78, 188.31, 52.94, 80.32, 65.49 and 25.25 MHz respectively using $SiMe_4$, 0.1 mol dm^{-3} LiCl(aq), CCl_3F, 1 mol dm^{-3} NaCl(aq), 85% H_3PO_4 1 mol dm^{-3} RbCl(aq) and 0.1 mol dm^{-3} CsCl(aq) as references (δ 0.0). The IR spectra were recorded in solution (CH_2Cl_2) on a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses were carried out at the Chemistry Department, University of Manchester Institute of Science and Technology.

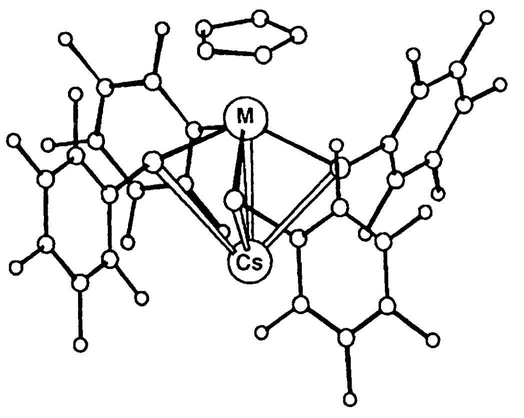


Fig. 5 Possible structure of $Cs[M(SC_6F_5)_4(cp)]$ **3** showing sulfur co-ordination

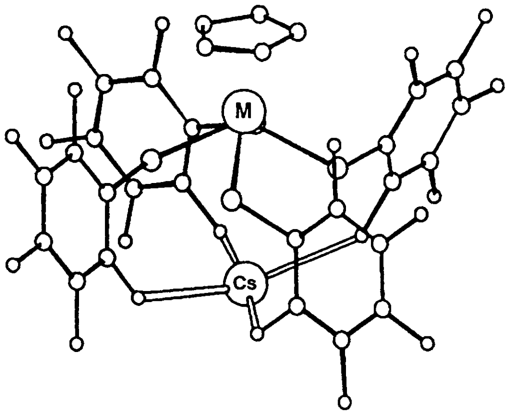


Fig. 6 Possible structure of $Cs[M(SC_6F_5)_4(cp)]$ **3** showing fluorine co-ordination

Preparation of $[W(SC_6F_5)(CO)_3(cp)]$.—The compound $[\{W(CO)_3(cp)\}_2]$[19] (1.057 g, 1.59 mmol) and $C_6F_5SSC_6F_5$ (631 mg, 1.59 mmol) were photolysed in toluene (60 cm^3) with a medium-pressure mercury lamp for 12 h. The solution was pumped to dryness and chromatographed on Florisil with 10% diethyl ether–light petroleum. The solution was concentrated *in vacuo* and cooled to −15 °C to afford orange crystals of $[W(SC_6F_5)(CO)_3(cp)]$ (1.015 g, 60%) which were identified by comparison of the IR spectrum with published data.[20]

Reaction of $Tl[Mo(SC_6F_5)_2(CO)_2(cp)]$ *with* $C_6F_5SSC_6F_5$.—The compound $Tl[Mo(SC_6F_5)_2(CO)_2(cp)]$ (100 mg, 0.12 mmol) and $C_6F_5SSC_6F_5$ (44 mg, 0.12 mmol) were photolysed in thf (40 cm^3) with a medium-pressure mercury lamp for 18 h. The solution was pumped to dryness and extracted into dichloromethane. This was filtered, centrifuged and concentrated *in vacuo*. Light petroleum (*ca.* 10 cm^3) was added and the solution cooled to −15 °C to afford red microcrystals of $Tl[Mo(SC_6F_5)_4(cp)]$ **1a** (72 mg, 56%) which were identified by comparison with an authentic sample.[1]

Reaction of $[W(SC_6F_5)(CO)_3(cp)]$ *with* 4 *Equivalents of* $Tl(SC_6F_5)$.—The compound $[W(SC_6F_5)(CO)_3(cp)]$ (51 mg, 0.096 mmol) and $Tl(SC_6F_5)$ (164 mg, 0.04 mmol) were photolysed in thf (40 cm^3) with a medium-pressure mercury lamp for 4 d. The solution was pumped to dryness and extracted

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* We thank a referee for drawing this to our attention.

into dichloromethane. This was filtered, centrifuged and concentrated *in vacuo*. Light petroleum (*ca.* 10 cm^3) was added and the solution cooled to −15 °C to afford the yellow powder $Tl[W(SC_6F_5)_4(cp)]$ **1b** (3 mg, 3%) which was identified by comparison with an authentic sample.

Improved Synthesis of $[W(SC_6F_5)_3(CO)(cp)]$ **2**: *Reaction of* $[WBr_3(CO)_2(cp)]$ *with* $3Tl(SC_6F_5)$.—The compound $[WBr_3(CO)_2(cp)]$[16] (1.68 g, 4.08 mmol) and $Tl(SC_6F_5)$ (5.00 g, 12.39 mmol) were stirred in dichloromethane (40 cm^3) under nitrogen at room temperature (r.t.) for 6 d. The dark solution was filtered, centrifuged and concentrated *in vacuo*. Light petroleum (*ca.* 10 cm^3) was added and the solution cooled to −15 °C affording dark green crystals of $[W(SC_6F_5)_3(CO)(cp)]\cdot 0.5CH_2Cl_2$. These were recrystallised a second time from dichloromethane–hexane to give crystals of the product (2.24 g, 60%) which were identified by comparison with an authentic sample.

Reaction of $[MoI_3(CO)_2(cp)]$ *with 5 Equivalents of* $Cs(SC_6F_5)$.—The compound $[MoI_3(CO)_2(cp)]$ (0.25 g, 0.4 mmol) was treated with thf (40 cm^3) under N_2 with 5 equivalents of $Cs(SC_6F_5)$ (0.7 g, 2.1 mmol) when the solution turned orange. After 6 d the reaction was stopped and the thf completely removed under vacuum. The residue was extracted with CH_2Cl_2 (40 cm^3) and filtered. The clear orange solution was reduced in volume under vacuum and light petroleum added before cooling to −15 °C when a dark oil separated. The remaining solution was separated from the oil and solvent removed completely under vacuum. The resulting residue was dissolved in diethyl ether, centrifuged to remove a fine white suspension and the volume reduced *in vacuo*. Light petroleum (*ca.* 10 cm^3) was then added before cooling to −15 °C. After several days bright red-orange microcrystals formed which were washed with light petroleum (*ca.* 10 cm^3) and dried under vacuum to give $Cs[Mo(SC_6F_5)_4(cp)]$ **3a** (39 mg, 9%) (Found: C, 31.8; H, 0.7; S, 11.8. $C_{29}H_5CsF_{20}MoS_4$ requires C, 31.9; H, 0.5; S, 11.7%). IR($CHCl_3$): C_6F_5 vibrations at 1511 and 1477 cm^{-1}. NMR: $^1H(CDCl_3)$ δ 5.40 (s, 5 H, C_5H_5); $^{19}F(CDCl_3)$ δ −131.8 (br m, 8 *o*-F), −155.4 (t, 4, *p*-F), −162.2 (br, 8 *m*-F); (CD_2Cl_2, 20 °C) δ −131.8 (br, 8 *o*-F), −156.8 (t, 4 *p*-F), −162.2 (br m, 8 *m*-F, coalescence at −17 °C); (CD_2Cl_2, −60 °C) δ −131.4 [octet of m, 4 *o*-F, *J*(Cs–F) 58.6], −131.6 (dd, 4 *o*-F), −155.6 (t, 4 *p*-F), −161.2 (m, 4 *m*-F), −163.4 (m, 4 *m*-F); ($CD_3C_6D_5$, 40 °C) δ −132.2 [octet, 8*o*-F, *J*(Cs–F) 29.7], − 156.6 (t, 4 *p*-F), −163.2 (m, 8 *m*-F, coalescence at −17 °C); ($CD_3C_6D_5$, −60 °C) δ −131.5 (dd, 4 *o*-F), −132.2 (br m, 4 *o*-F), −155.4 (t, 4 *p*-F), −160.5 (m, 4 *m*-F), −164.0 (m, 4 *m*-F); [$(CD_3)_2CO$, 19 °C] δ −130.5 (m, 8 *o*-F, coalescence at −50 °C), −160.3 (t, 4 *p*-F), −165.9 (m, 8 *m*-F, coalescence at −65 °C); [$(CD_3)_2CO$, −80 °C] δ −128.0 (d, 4 *o*-F), −132.6 (d, 4 *o*-F), −158.5 (t, 4 *p*-F), −164.0 (m, 4 *m*-F), −165.0 (m, 4 *m*-F); ^{133}Cs (CD_2Cl_2, 30 °C) δ −15.1 (s); (CD_2Cl_2, −60 °C) δ −0.49 [quintet, *J*(Cs–F) 57.6]; ($CD_3C_6D_5$, −20 °C) δ −79.5 [nonet, *J*(Cs–F) 29.7]; ($CD_3C_6D_5$, −60 °C) δ −82.0 [quintet, *J*(Cs–F) 57.8 Hz].

Reaction of $[WI_3(CO)_2(cp)]$ *with 5 Equivalents of* $Cs(SC_6F_5)$.—The compound $[WI_3(CO)_2(cp)]$ (0.2819 g, 0.4 mmol) was treated with 5 equivalents of $Cs(SC_6F_5)$ (0.6425 g, 1.9 mmol) in thf (50 cm^3) under N_2 when the solution turned lighter and more yellow. After 3 d the reaction was stopped and the solvent removed under vacuum. The residue was extracted with CH_2Cl_2 (40 cm^3) and filtered. The pale orange solution was reduced in volume *in vacuo* and light petroleum (*ca.* 10 cm^3) added before cooling to −15 °C. A white suspension of unreacted $Cs(SC_6F_5)$ was removed by filtration. More light petroleum was added and on recooling to −15 °C a yellow powder formed. This was recrystallized from diethyl ether–light petroleum at −15 °C to give bright yellow microcrystals of $Cs[W(SC_6F_5)_4(cp)]$ **3d** (34 mg, 10%) (Found: C, 29.9; H, 0.4; S, 10.9. $C_{29}H_5CsF_{20}S_4W$ requires C, 29.6; H, 0.4; S, 10.9%). IR ($CHCl_3$): C_6F_5 vibrations at 1511 and 1477 cm^{-1}. NMR: ^1H ($CDCl_3$) δ 5.35 (s, 5 H, C_5H_5); ^{19}F ($CDCl_3$) δ −131.8 (br, 8 *o*-F), −155.5 (t, 4 *p*-F), −162.2 (br, 8 *m*-F); (CD_2Cl_2, 20 °C) δ −132.0 (br, 8 *o*-F), −156.8 (t, 4 *p*-F), −163.0 (br, 8 *m*-F, coalescence at −3 °C); (CD_2Cl_2, −60 °C) δ −131.0 [d of octet, 4 *o*-F, *J*(Cs–F) 61.1, *J*(F–F) 28], −132.0 (dd, 4 *o*-F), −155.6 (t, 4 *p*-F), −161.0 (m, 4 *m*-F), −163.5 (m, 4 *m*-F); ($CD_3C_6D_5$, 20 °C) δ −132.20 (octet, 8 *o*-F), −156.4 (t, 4 *p*-F), −163.0 (br, 8 *m*-F, coalescence at −3 °C); ($CD_3C_6D_5$, −60 °C), δ −131.5 (br m, 4 *o*-F), −132.0 (dd, 4 *o*-F), −155.3 (t, 4 *p*-F), −160.3 (m, 4 *m*-F), −163.9 (m, 4 *m*-F); ^{133}Cs (CD_2Cl_2, −60 °C) δ 2.3 [quintet, *J*(Cs–F) 60.5 Hz].

Reactions of $[W(SC_6F_5)_3(CO)(cp)]$ **2**.—*With* $Cs(SC_6F_5)$. Compound **2** (122 mg, 0.14 mmol) and $Cs(SC_6F_5)$ (93 mg, 0.28 mmol) were stirred in thf (30 cm^3) at r.t. for 2 h giving a red solution. The solvent was completely removed *in vacuo* and the residue extracted with diethyl ether. The yellow solution was filtered, reduced in volume, mixed with hexane (*ca.* 10 cm^3) and centrifuged to remove unreacted $Cs(SC_6F_5)$ and cooled at −15 °C to afford yellow microcrystals of $Cs[W(SC_6F_5)_4(cp)]$ **3d** (21 mg, 13%).

With $Li(SC_6F_5)$. Compound **2** (200 mg, 0.22 mmol) and $Li(SC_6F_5)$ (42 mg, 0.20 mmol) were stirred in thf (30 cm^3) at r.t. for 10 min giving a rust coloured solution. The solvent was removed *in vacuo* and the residue extracted with hexane. The yellow solution was filtered, concentrated *in vacuo* and cooled to −15 °C to afford green-yellow crystals of $[Li(thf)_4][W(SC_6F_5)_4(cp)]$ **4a** (65 mg, 22%). IR(CH_2Cl_2): C_6F_5 vibrations at 1511s and 1486s cm^{-1}. NMR: $^1H(C_6D_6$, 20 °C) δ 5.32 (s, 5 H, C_5H_5), 3.55 (m, 16 H, thf) and 1.4 (m, 16 H, thf); $^{19}F(CD_2Cl_2$, 20 °C) δ −133.29 (m, 8 *o*-F), −157.63 (t, 4 *p*-F) and −164.01 (m, 8 *m*-F); (CD_2Cl_2, −80 °C) δ −130.41 (br d, 4 *o*-F), −133.12 (dd, 4 *o*-F), −156.82 (t, 4 *p*-F), −162.48 (m, 4 *m*-F), −164.57 (m, 4 *m*-F).

With $Na(SC_6F_5)$. Compound **2** (140 mg, 0.16 mmol) and $Na(SC_6F_5)$ (38 mg, 0.17 mmol) were stirred in thf (30 cm^3) at r.t. for 2 h giving a red solution. The solvent was removed *in vacuo* and the residue extracted with diethyl ether. The yellow solution was filtered, reduced in volume, mixed with hexane (*ca.* 10 cm^3), and cooled to −15 °C to afford yellow microcrystals of $[Na(thf)][W(SC_6F_5)_4(cp)]$ **4b** (107 mg, 63%) (Found: C, 34.2; H, 1.1; S, 10.5. $C_{33}H_{13}F_{20}NaOS_4W$ requires C, 34.7; H, 1.1; S, 11.2%). IR (CH_2Cl_2): C_6F_5 vibrations at 1510s and 1486s cm^{-1}. NMR: $^1H(C_6D_6$, 20 °C) δ 5.13 (s, 5 H, C_5H_5), 3.55 (m, 4 H, thf) and 1.4 (m, 4 H, thf); $^{19}F(CD_2Cl_2$, 19 °C) δ −136.6 (br, 8 *o*-F), −156.16 (t, 4 *p*-F), −162.85 (br m, 8 *m*-F); (CD_2Cl_2, −60 °C) δ −133.48 (br d, 4 *o*-F), −138.94 (br d, 4 *o*-F), −155.15 (t, 4 *p*-F), −160.73 (m, 4 *m*-F), −163.14 (m, 4 *m*-F); $^{23}Na(CD_2Cl_2$, 19 °C), δ −9.36 (br); (CD_2Cl_2, −60 °C) δ 27.17 (br).

With $K(SC_6F_5)$. Compound **2** (158 mg, 0.18 mmol) and $K(SC_6F_5)$ (86 mg, 0.18 mmol) were stirred together in thf (40 cm^3) for 12 h when the dark green solution turned orange-yellow. The solution was evaporated to dryness and extracted into diethyl ether, filtered, centrifuged and concentrated *in vacuo*. Light petroleum was added and the solution cooled to −15 °C to give yellow crystals of $K[W(SC_6F_5)_4(cp)]$ **3b** (57 mg, 29%) (Found: C, 32.4; H, 0.7; S, 11.4. $C_{29}H_5F_{20}KS_4W$ requires C, 32.1; H, 0.5; S, 11.8%). NMR: $^1H(CDCl_3$, 20 °C) δ 5.32 (s, 5 H, C_5H_5); $^{19}F(CD_2Cl_2$, 19 °C) δ −135.0 (br, 8 *o*-F), −156.54 (t, 4 *p*-F), −163.10 (br, 8 *m*-F); (CD_2Cl_2, −80 °C) δ −132.80 (dd, 4 *o*-F), −135.59 (dd, 4 *o*-F), −155.22 (t, 4 *p*-F), −160.73 (t, 4 *m*-F), −163.20 (t, 4 *m*-F).

With $Rb(SC_6F_5)$.Compound **2** (179 mg, 0.21 mmol) and $Rb(SC_6F_5)$ (96 mg, 0.34 mmol) were stirred together in thf (40 cm^3) for 12 h when the dark green solution turned orange-yellow. The solution was evaporated to dryness and extracted into diethyl ether, filtered, centrifuged and concentrated *in vacuo*. Light petroleum was added and the solution cooled to −15 °C to give opaque yellow crystals of $Rb[W(SC_6F_5)_4(cp)]$ **3c** (90 mg, 39%) (Found: C, 30.9; H, 0.4; S, 11.1. $C_{29}H_5F_{20}$-

RbS$_4$W requires C, 30.8; H, 0.5; S, 11.3%). NMR: ^{1}H(CDCl$_3$, 20 °C) δ 5.27 (s, 5 H, C$_5$H$_5$); ^{19}F(CD$_2$Cl$_2$, 20 °C) δ −133.95 (br, 8 *o*-F), −156.58 (t, 4 *p*-F), −163.12 (br, 8 *m*-F); (CD$_2$Cl$_2$, −60 °C) δ −132.46 (dd, 4 *o*-F), −134.56 (dd, 4 *o*-F), −155.41 (t, 4 *p*-F), −160.88 (m, 4 *m*-F), −163.33 (m, 4 *m*-F).

Synthesis of Na[W(SC$_6$F$_5$)$_4$(cp)].—Compound [W(SC$_6$F$_5$)$_3$(CO)(cp)] **2** (368 mg, 0.42 mmol) and Na(SC$_6$F$_5$) (93 mg, 0.42 mmol) were stirred together in thf (40 cm^3) for 12 h. The resulting solution was evaporated to dryness and extracted into diethyl ether, filtered, centrifuged and evaporated to dryness once again. Further extractions into dichloromethane followed by evaporation to dryness were carried out to remove any co-ordinated thf. Finally recrystallization was effected from dichloromethane–light petroleum at −15 °C giving a bright yellow powder, Na[W(SC$_6$F$_5$)$_4$(cp)] (210 mg, 47%) (Found: C, 32.9; H, 0.7; S, 12.0. C$_{29}$H$_5$F$_{20}$NaS$_4$W requires C, 32.6; H, 0.5; S, 12.0%).

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