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

Jack L. Davidson,* Calum H. McIntosh, Pascal C. Leverd, W. Edward Lindsell* and Nigel J. Simpson

Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, UK

The photochemical reaction of TI[Mo(SC₆F₅)₂(CO)₂(cp)] (cp = η^5 -C₅H₅) with C₆F₅SSC₆F₅ in tetrahydrofuran (thf) solution affords the tetrathiolate TI[Mo(SC₆F₅)₄(cp)]. Similarly the photochemical reaction of [W(SC₆F₅)(CO)₃(cp)] with 4 equivalents of TI(SC₆F₅) gave TI[W(SC₆F₅)₄(cp)] in low yield. Reactions of [MI₃(CO)₂(cp)] (M = Mo or W) and [W(SC₆F₅)₃(CO)(cp)] with M'(SC₆F₅) in thf solution gave the ionic derivatives Cs[Mo(SC₆F₅)₄(cp)], M'[W(SC₆F₅)₄(cp)] (M' = Cs, Rb or K) and the solvated derivatives [M'(thf)_n][W(SC₆F₅)₄(cp)] (M' = Li, n = 4; M' = Na, n = 1). Fluorine-19 NMR studies reveal fluxional behaviour involving the C₆F₅ groups in all the derivatives. Dynamic ¹³³Cs and ¹⁹F NMR spectra of Cs[M(SC₆F₅)₄(cp)] in addition show coupling between caesium and four of the *ortho*-fluorines of the SC₆F₅ 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 molybdenum¹ and tungsten² derivatives Tl[M-(SC₆F₅)₄(cp)] (M = Mo **1a** or W **1b**, cp = η^5 -C₅H₅). X-Ray diffraction studies of **1a** and the [N(PPh₃)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 orthofluorines of the C_6F_5 groups) which can encapsulate a Tl⁺ ion. Variable-temperature ¹⁹F NMR spectra of $TI[M(SC_6F_5)_4(cp)]$ show solvent-dependent coupling between these four fluorines and ^{203/205}Tl. At higher temperatures fluxional motion involving the SC₆F₅ 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 coordination 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.

Results and Discussion

Previously we reported that the thallium derivative TI[Mo(SC₆F₅)₄(cp)] **1a** could be obtained by reaction of [MoCl(CO)₃(cp)] with >4 equivalents of Tl(SC₆F₅) in tetrahydrofuran (thf), a reaction which proceeds via the Mo^{II} intermediate Tl[Mo(SC₆F₅)₂(CO)₂(cp)].¹ However, the tungsten complex Tl[W(SC₆F₅)₄(cp)] **1b** required a tungsten(iv) precursor such as [WCl₃(CO)₂(cp)] and this reaction proceeds via the neutral monocarbonyl [W(SC₆F₅)₃(CO)(cp)].² It was of interest to extend the available routes to tetrathiolate anions [M(SC₆F₅)₄(cp)]⁻ and consequently the synthetic utility of carbonyl-containing intermediates was explored. It was subsequently found that the photochemical reaction of Tl[Mo(SC₆F₅)₂(CO)₂(cp)] with C₆F₅SSC₆F₅ in thf solution affords the tetrathiolate **1a** in 56% yield (Scheme 1). The photochemical reaction of Tl(SC₆F₅) similarly gave very small quantities



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

(3% yield) of the tungsten complex Tl[W(SC₆F₅)₄(cp)] **1b** (Scheme 1). Both of these reactions presumably proceed *via* photoejection of a carbonyl ligand thus allowing attack by the SC₆F₅-containing reagents. Initially we assumed that our inability to obtain **1b** from the reaction of [W(SC₆F₅)(CO)₃(cp)] with Tl(SC₆F₅) 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(SC₆F₅)-(CO)₃(cp)] towards CO loss⁴ 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 $[NBu_{4}^{n}]^{+2}$ it was anticipated that such species might afford a route to new metal derivatives by simple cation-exchange reactions. However, reactions of Tl[Mo(SC₆F₅)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 C₆F₅-containing species, the spectra of which were of insufficient quality to allow deductions concerning the nature of the components produced and workup 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 $[NBu_4^n][Mo-(SC_6F_5)_4(cp)]$ 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 [MoI₃(CO)₂(cp)] with Rb(SC₆F₅) or $Li(SC_6F_5)$, $[MoCl_2(C_3H_5)(CO)(cp)]$ ($\overline{C_3H_5}$ = 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(SC₆F₅) 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 reported² 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

$$[WBr_{3}(CO)_{2}(cp)] + 3Tl(SC_{6}F_{5}) \longrightarrow$$
$$[W(SC_{6}F_{5})_{3}(CO)(cp)] 2 \quad (1)$$

$$\mathbf{2} + \operatorname{Tl}(\operatorname{SC}_6\operatorname{F}_5) \longrightarrow \operatorname{Tl}[\operatorname{W}(\operatorname{SC}_6\operatorname{F}_5)_4(\operatorname{cp})] \mathbf{1b} \qquad (2)$$

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 crystallisation according to ¹H NMR spectroscopy but the crystallisation according to ¹H NMR spectroscopy but the crystallisation 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,<math>n = 44a(22%); M' = Na, n = 14b(63%)] which, in the case of M' = Na, could be converted to the thf-free species on repeated recrystallisation from dichloromethane. Solvation is confirmed



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

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 ¹⁹F NMR data for this compound were consistent with the formulation [Li(thf)₄][W(SC₆F₅)₄(cp)].

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 ¹³³Cs and ¹⁹F 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 ¹³³Cs and ¹⁹F. Thus, at 20 °C and above in $CD_3C_6D_5$ the ¹³³Cs NMR spectrum of $Cs[Mo(SC_6F_5)_4(cp)]$ 3a consists of a seven-line multiplet near $\delta - 80$. 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 coordinated 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-C₆F₅ 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 ¹⁹F NMR spectrum are observed over the temperature range 40 to -80 °C. At 40 °C one set of ortho-, meta- and parafluorine 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-(SC₆F₅)₄(cp)] **3a**: (a) - 20 °C, CD₃C₆D₅; (b) - 60 °C, CD₃C₆D₅

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 CD₂Cl₂ 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 CD₂Cl₂ the ¹³³Cs NMR spectrum of **3a** consists of a singlet, $\delta - 15.1$, 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 ¹⁹F NMR spectrum at room temperature no coupling to ¹³³Cs 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 C₆F₅ 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.

In deuteriated acetone at room temperature three well resolved multiplets due to freely rotating C_6F_5 groups are



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-(SC₆F₅)₄(cp)] 3a: (a) 20 °C, CD₂Cl₂; (b) - 60 °C, CD₂Cl₂

observed in the ¹⁹F 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 ¹⁹F 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 $Cs[Mo(SC_6F_5)_4(cp)]$ 3a $(-60 \text{ °C}, CD_2Cl_2)$ with expansion of the C_6F_5 ortho-fluorine resonances

To summarise it appears that in $CD_3C_6D_5$ 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 ¹³³Cs 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_2Cl_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 coordinated 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_2Cl_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 ¹⁹F 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 ΔG^{\ddagger} for C₆F₅ fluxional motion were calculated from coalescence temperatures of the meta- and in some cases, the ortho-fluorine peaks.

Barriers (ΔG^{\ddagger}) to rotation/inversion for C_6F_5 rings for each complex in CD_2Cl_2 are: K[W(SC₆F₅)₄(cp)] **3b** $(\Delta G^{\ddagger}_{276} =$ 51.5 ± 0.5 kJ mol⁻¹), Rb[W(SC₆F₅)₄(cp)] **3c** $(\Delta G^{\ddagger}_{278} =$ 52.1 ± 0.5 kJ mol⁻¹) and Cs[W(SC₆F₅)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(SC₆F₅)₄(cp)] and $\Delta G^{\ddagger}_{229} =$ 43.4 ± 0.5 kJ mol⁻¹ for [N(PPh_3)_2][W(SC₆F₅)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 coordination is unambiguous, has a relatively small value $(\Delta G_{248}^{\dagger} = 46.7 \pm 0.8 \text{ kJ mol}^{-1})$. A similar value was obtained for the sodium compound [Na(thf)][W(SC₆F₅)₄(cp)] **4b** $(\Delta G_{255}^{\dagger} = 46.6 \pm 0.3 \text{ kJ mol}^{-1})$. The ²³Na NMR spectrum of this compound was also recorded and at 19 °C shows a broad single resonance at $\delta - 9.36$. 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 ²³Na.

Interestingly, the ¹⁹F NMR spectrum of the lithium derivative 4a in CD₂Cl₂ 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 \pm 5 K for both the ortho- and metafluorine resonances which correspond to a barrier to rotation for C_6F_5 rings of 41.3 \pm 0.8 kJ mol⁻¹. This barrier is even lower than that of $[N(PPh_3)_2][W(SC_6F_5)_4(cp)]$. 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 ¹H NMR spectrum of the yellow powder obtained showed the absence of thf, and a single sharp peak was obtained in the ⁷Li NMR at δ 0.04 at -60 °C in CD₂Cl₂, the ¹⁹F 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 ¹H NMR data, was successful in removing the thf solvate from the crystal, but again the ¹⁹F NMR spectrum indicated that several species were present in solution.

Interestingly, we note that variable-temperature ¹³³Cs 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 $[M(SC_6F_5)_4(cp)]^-$ 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 ¹³³Cs and ¹⁹F 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 $[M(SC_6F_5)_4(cp)]^-$ ligand.

Conclusion

The use of transition-metal complexes containing terminal thiolate ligands to co-ordinate other transition metals is well established⁷ but co-ordination to alkali metals is, to our knowledge, unknown. As described earlier the thallium in $Tl[Mo(SC_6F_5)_4(cp)]$ 1a is co-ordinated primarily via the sulfurs, the interaction with four ortho-fluorines being essentially non-bonding. In contrast, the related Ru-SC₆F₅ chelate ring in $[Ru(SC_6F_4F-2)(SC_6F_5)_2(PMe_2Ph)_2]$ 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_6F_5 groups. This question is not fully resolved by the NMR data which do not directly distinguish between the sulfur coordinated 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 C₆F₅ ortho-fluorines, presumably via rotation of

2427

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 coordination 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 TI^+ against K⁺ and Rb⁺.¹¹ On this basis binding was suggested to occur at the sulfurs of the tri-u-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]aneS₃) 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 PF₆⁻ 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 ethers¹³ 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 known¹⁵ 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 $TI[Mo(SC_6F_5)_2-(CO)_2(cp)]$,¹ [NBuⁿ₄][Mo(SC_6F_5)_4(cp)],² [MoI_3(CO)_2-(cp)],¹⁶[WI_3(CO)_2(cp)],¹⁶TI(SC_6F_5),¹C_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(PPh₃)₂]Cl were obtained commercially (BDH, Aldrich, Ventron), and used as supplied. Proton, ⁷Li, ¹⁹F, ²³Na, ³¹P, ⁸⁷Rb and ¹³³Cs 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 SiMe₄, 0.1 mol dm⁻³



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

LiCl(aq), CCl₃F, 1 mol dm⁻³ NaCl(aq), 85% H₃PO₄ 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 (CH₂Cl₂) 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.

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 cm³) 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(SC₆F₅)₂(CO)₂(cp)] with C₆F₅SSC₆F₅.— The compound Tl[Mo(SC₆F₅)₂(CO)₂(cp)] (100 mg, 0.12 mmol) and C₆F₅SSC₆F₅ (44 mg, 0.12 mmol) were photolysed in thf (40 cm³) 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 cm³) was added and the solution cooled to -15 °C to afford red microcrystals of Tl[Mo(SC₆F₅)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 $TI(SC_6F_5)$.—The compound $[W(SC_6F_5)(CO)_3(cp)]$ (51 mg, 0.096 mmol) and $TI(SC_6F_5)$ (164 mg, 0.04 mmol) were photolysed in thf (40 cm³) with a medium-pressure mercury lamp for 4 d. The solution was pumped to dryness and extracted

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

into dichloromethane. This was filtered, centrifuged and concentrated *in vacuo*. Light petroleum (*ca.* 10 cm³) was added and the solution cooled to -15 °C to afford the yellow powder Tl[W(SC₆F₅)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 cm³) under nitrogen at room temperature (r.t.) for 6 d. The dark solution was filtered, centrifuged and concentrated *in vacuo*. Light petroleum (*ca.* 10 cm³) was added and the solution cooled to -15 °C affording dark green crystals of $[W(SC_6F_5)_3(CO)(cp)]$ -0.5CH₂Cl₂. 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 [MoI₃(CO)₂(cp)] (0.25 g, 0.4 mmol) was treated with thf (40 cm³) 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 cm³) 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 cm³) was then added before cooling to -15 °C. After several days bright red-orange microcrystals formed which were washed with light petroleum (ca. 10 cm³) 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. C₂₉H₅CsF₂₀MoS₄ requires C, 31.9; H, 0.5; S, 11.7%). IR(CHCl₃): C₆F₅ vibrations at 1511 and 1477 cm⁻¹. NMR: ¹H(CDCl₃) δ 5.40 (s, 5 H, C₅H₅); ¹⁹F(CDCl₃) $\delta - 131.8$ (br m, 8 o-F), -155.4 (t, 4, p-F), -162.2 (br, 8 m-F); $(CD_2Cl_2, 20 °C) \delta -131.8 (br, 8 o-F), -156.8 (t, 4 p-F),$ -162.2 (br m, 8 *m*-F, coalescence at -17 °C); (CD₂Cl₂, -60 °C) $\delta -131.4$ [octet of m, 4 o-F, J(Cs-F) 58.6], -131.6(dd, 4o-F), -155.6(t, 4p-F), -161.2(m, 4m-F), -163.4(m, 4m-F))*m*-F); $(CD_3C_6D_5, 40 \text{ °C}) \delta - 132.2 \text{ [octet, } 80\text{-}\text{F}, J(Cs\text{-}\text{F}) 29.7\text{]},$ 156.6 (t, 4 p-F), -163.2 (m, 8 m-F, coalescence at -17 °C); $(CD_3C_6D_5, -60 \,^{\circ}C) \,\delta - 131.5 \,(dd, 4 \,o\text{-F}), -132.2 \,(br m, 4)$ o-F), -155.4 (t, 4 p-F), -160.5 (m, 4 m-F), -164.0 (m, 4 m-F); $[(CD_3)_2CO, 19 °C] \delta -130.5$ (m, 8 o-F, coalescence at -50 °C), -160.3 (t, 4 p-F), -165.9 (m, 8 m-F, coalescence at -65 °C; [(CD₃)₂CO, -80 °C] $\delta -128.0$ (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 (CD₂Cl₂, 30 °C) δ -15.1 (s); (CD₂Cl₂, -60 °C) $\delta = 0.49$ [quintet, J(Cs-F) 57.6]; (CD₃C₆D₅, -20 °C) $\delta = 79.5$ [nonet, J(Cs-F) 29.7]; (CD₃C₆D₅, -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 cm³) under N₂ 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 cm³) and filtered. The pale orange solution was reduced in volume *in vacuo* and light petroleum (*ca.* 10 cm³) 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

J. CHEM. SOC. DALTON TRANS. 1994

(CHCl₃): C₆F₅ vibrations at 1511 and 1477 cm⁻¹. NMR: ¹H (CDCl₃) δ 5.35 (s, 5 H, C₅H₅); ¹⁹F (CDCl₃) δ -131.8 (br, 8 *o*-F), -155.5 (t, 4 *p*-F), -162.2 (br, 8 *m*-F); (CD₂Cl₂, 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); (CD₂Cl₂, -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); (CD₃C₆D₅, 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); (CD₃C₆D₅, -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); ¹³³Cs (CD₂Cl₂, -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 cm³) 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 cm³) 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(SC₆F₅). Compound 2 (200 mg, 0.22 mmol) and Li(SC₆F₅) (42 mg, 0.20 mmol) were stirred in thf (30 cm³) 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-(SC₆F₅)₄(cp)] **4a** (65 mg, 22%). IR(CH₂Cl₂): C₆F₅ vibrations at 1511s and 1486s cm⁻¹. NMR: ¹H(C₆D₆, 20 °C) δ 5.32 (s, 5 H, C₅H₅), 3.55 (m, 16 H, thf) and 1.4 (m, 16 H, thf); ¹⁹F(CD₂Cl₂, 20 °C) δ -133.29 (m, 8 *o*-F), -157.63 (t, 4 *p*-F) and -164.01 (m, 8 *m*-F); (CD₂Cl₂, -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(SC₆F₅). Compound 2 (140 mg, 0.16 mmol) and Na(SC₆F₅) (38 mg, 0.17 mmol) were stirred in thf (30 cm³) 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 cm³), and cooled to -15 °C to afford yellow microcrystals of [Na(thf)][W(SC₆F₅)₄(cp)] **4b** (107 mg, 63%) (Found: C, 34.2; H, 1.1; S, 10.5. C₃₃H₁₃F₂₀NaOS₄W requires C, 34.7; H, 1.1; S, 11.2%). IR (CH₂Cl₂): C₆F₅ vibrations at 1510s and 1486s cm⁻¹. NMR: ¹H(C₆D₆, 20 °C) δ 5.13 (s, 5 H, C₅H₅), 3.55 (m, 4 H, thf) and 1.4 (m, 4 H, thf); ¹⁹F(CD₂Cl₂, 19 °C) δ - 136.6 (br, 8 *o*-F), -156.16 (t, 4 *p*-F), -162.85 (br m, 8 *m*-F); (CD₂Cl₂, -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); ²³Na(CD₂Cl₂, 19 °C), δ -9.36 (br); (CD₂Cl₂, -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 cm³) for 12 h when the dark green solution turned orangeyellow. 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(CDCl₃, 20 °C) δ 5.32 (s, 5 H, C₅H₅); ¹⁹F(CD₂Cl₂, 19 °C) δ –135.0 (br, 8 *o*-F), -156.54 (t, 4 *p*-F), -163.10 (br, 8 *m*-F); (CD₂Cl₂, -80 °C) δ –132.80 (dd, 4 *o*-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 cm³) for 12 h when the dark green solution turned orangeyellow. 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. $C_{29}H_5F_{20}$ - RbS₄W requires C, 30.8; H, 0.5; S, 11.3%). NMR: ¹H(CDCl₃, 20 °C) δ 5.27 (s, 5 H, C₅H₅); ¹⁹F(CD₂Cl₂, 20 °C) δ -133.95 (br, 8 *o*-F), -156.58 (t, 4 *p*-F), -163.12 (br, 8 *m*-F); (CD₂Cl₂, -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(SC₆F₅)₄(cp)].—Compound [W(SC₆-F₅)₃(CO)(cp)] **2** (368 mg, 0.42 mmol) and Na(SC₆F₅) (93 mg, 0.42 mmol) were stirred together in thf (40 cm³) 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 coordinated thf. Finally recrystallization was effected from dichloromethane–light petroleum at -15 °C giving a bright yellow powder, Na[W(SC₆F₅)₄(cp)] (210 mg, 47%) (Found: C, 32.9; H, 0.7; S, 12.0. C₂₉H₅F₂₀NaS₄W requires C, 32.6; H, 0.5; S, 12.0%).

Acknowledgements

We thank the SERC for financial support (to N. J. S. and C. H. Mcl.) and Dr. A. S. F. Boyd for running the NMR spectra.

References

- I W. A. W. A. Bakar, J. L. Davidson, W. E. Lindsell, K. J. McCullough and K. W. Muir, J. Chem. Soc., Dalton Trans., 1989, 991.
- 2 W. A. W. A. Bakar, J. L. Davidson, W. E. Lindsell and K. J. McCullough, J. Chem. Soc., Dalton Trans., 1990, 61.
- 3 A. S. F. Boyd, J. L. Davidson, C. H. McIntosh, P. C. Leverd and W. E. Lindsell, J. Chem. Soc., Dalton Trans., 1992, 2531.
- 4 R. Havlin and G. R. Knox, Z. Naturforsch., Teil B, 1966, 21, 1108.

- 5 J. L. Davidson, W. E. Lindsell, K. J. McCullough and C. H. McIntosh, unpublished work.
- 6 E. Mei, A. I. Popov and J. L. Dye, J. Am. Chem. Soc., 1977, 99, 6532; E. Kaufmann, J. L. Dye, J.-M. Lehn and A. I. Popov, J. Am. Chem. Soc., 1980, 102, 2274.
- 7 T. A. Wark and D. W. Stephan, Organometallics, 1989, 8, 2836;
 W. E. Douglas and M. L. H. Green, J. Chem. Soc., Dalton Trans., 1972, 1796; P. S. Braterman, V. A. Wilson and K. K. Joshi, J. Chem. Soc. A, 1971, 191.
- 8 R. M. Catala, D. Cruz-Garritz, A. Hills, R. L. Richards, P. Sosa and H. Torrens, J. Chem. Soc., Chem. Commun., 1987, 261.
- 9 D. J. Cram, S. B. Brown, T. Taguchi, M. Freigel, E. Maverick and K. N. Trueblood, J. Am. Chem. Soc., 1984, 106, 695; D. J. Cram, Angew. Chem., Int. Ed. Engl., 1986, 25, 1039.
- 10 U. Pieper, S. Walter, U. Klingebiel and D. Stalke, Angew. Chem., Int. Ed. Engl., 1990, 29, 209.
- 11 A. H. Hoveyada, Z. Xu, J. P. Morken and A. F. Houri, J. Am. Chem. Soc., 1991, 113, 8950.
- 12 A. J. Blake, J. A. Greig and M. Schroder, J. Chem. Soc., Dalton Trans., 1991, 529.
- A. V. Bajaj and N. S. Poonia, *Coord. Chem. Rev.*, 1988, 87, 55;
 C. J. Pedersen, *Angew. Chem., Int. Ed. Engl.*, 1988, 27, 1021;
 D. J. Cram, *Angew. Chem., Int. Ed. Engl.*, 1988, 25, 1009.
- 14 D. Barr, P. R. Raithby, P. von Rague Schleyer, R. Snaith and P. S. Wright, J. Chem. Soc., Chem. Commun., 1990, 643.
- 15 M. Y. Darensbourg, Prog. Inorg. Chem., 1985, 33, 221.
- 16 M. L. H. Green and W. E. Lindsell, J. Chem. Soc. A, 1967, 686.
- 17 P. Robson, M. Stacey, R. Stephens and J. Tatlow, J. Chem. Soc., 1960, 4754.
- 18 M. E. Peach, Can. J. Chem., 1968, 46, 2699.
- 19 R. Birdwhistell, P. Hackett and A. R. Manning, J. Organomet. Chem., 1978, 157, 239.
- 20 R. Havlin, Ph.D. Thesis, University of Strathclyde, 1967.

Received 5th April 1994; Paper 4/01996B