Co-ordination of Alkali Metals to Sulfur-based Organometallic Ligands: ^{133}Cs and ^{19}F Nuclear Magnetic Resonance Studies of Cs[Mo(SC_6F_5)$_4$(η^5-C_5H_5)], the First Example of Caesium–Fluorine Spin–Spin Coupling

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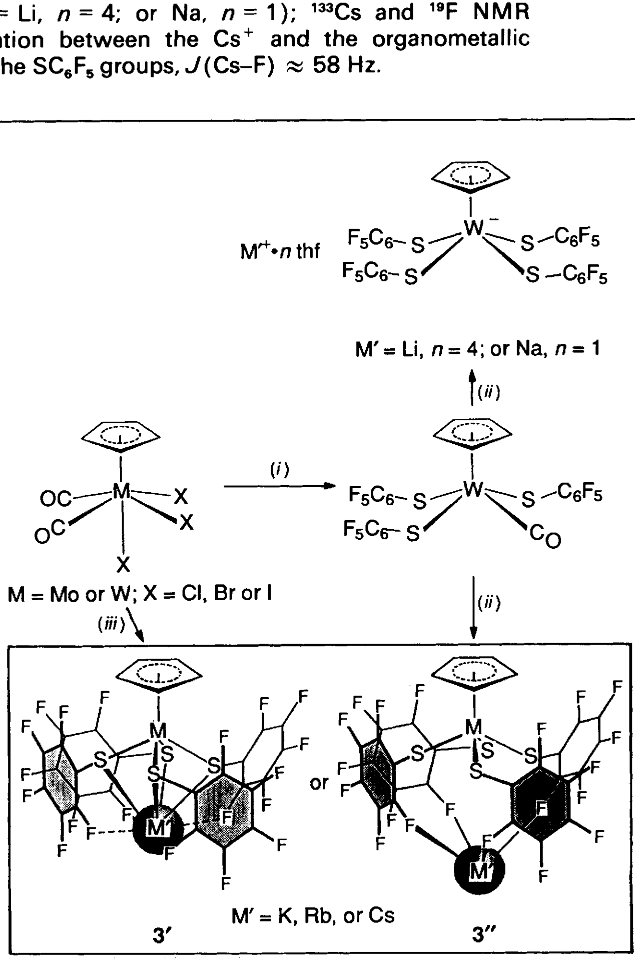
Reactions of the complexes [MoI$_3$(CO)$_2$(η^5-C_5H_5)] and [W(SC_6F_5)$_3$(CO)(η^5-C_5H_5)] with M′(SC_6F_5) give Cs[Mo(SC_6F_5)$_4$(η^5-C_5H_5)], M′[W(SC_6F_5)$_4$(η^5-C_5H_5)] (M′ = Cs, Rb or K) and solvated derivatives (M = Mo or W) M′[W(SC_6F_5)$_4$(η^5-C_5H_5)]·*n*thf (M′ = Li, *n* = 4; or Na, *n* = 1); ^{133}Cs and ^{19}F NMR studies of Cs[M(SC_6F_5)$_4$(η^5-C_5H_5)] reveal co-ordination between the Cs$^+$ and the organometallic anion and Cs–F coupling involving four *o*-fluorines of the SC_6F_5 groups, *J*(Cs–F) ≈ 58 Hz.

Recently we reported the syntheses and dynamic NMR studies of molybdenum[1] and tungsten[2] organometallic anions [M(SC_6F_5)$_2$$L_2$($\eta^5$-$C_5H_5$)]$^-$ (M = Mo, L = SC_6F_5 **1a** or CO; M = W, L = SC_6F_5 **1b**). X-Ray diffraction studies of A[Mo(SC_6F_5)$_4$(η^5-C_5H_5)] [A = Tl **2a** or N(PPh_3)$_2$] revealed that the 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)$_4$(η^5-C_5H_5)] (M = Mo **2a** or W **2b**) show solvent-dependent coupling between these four fluorines and $^{203/205}$Tl. At higher temperatures deco-ordination of the Tl$^+$ leads to loss of coupling, accompanied by the onset of fluxional motion involving the SC_6F_5 groups. We have now synthesised alkali-metal derivatives of **1** and report dynamic ^{133}Cs and ^{19}F NMR studies which show similar features to those of **2**, in particular spin–spin coupling involving the two nuclei.

Reactions of [MoI$_3$(CO)$_2$(η^5-C_5H_5)] and [W(SC_6F_5)$_3$(CO)(η^5-C_5H_5)] with M′(SC_6F_5) (see Scheme 1) in tetrahydrofuran (thf) at room temperature afford red Cs[Mo(SC_6F_5)$_4$(η^5-C_5H_5)] and yellow M′[W(SC_6F_5)$_4$(η^5-C_5H_5)] (M′ = Cs, Rb or K) as microcrystalline products after recrystallisation from diethyl ether or dichloromethane–light petroleum (b.p. 60–80 °C) at −15 °C, in 10–40% isolated yields.† In contrast, derivatives M′[W(SC_6F_5)$_4$(η^5-C_5H_5)]·*n*thf [M′ = Li, *n* = 4 (22%) or Na, *n* = 1 (63%)] were obtained as solvates which, in the case of M′ = Na, could be converted into the thf-free species on repeated recrystallisation.†

The ^{133}Cs and ^{19}F NMR spectra ‡ of the caesium derivatives Cs[M(SC_6F_5)$_4$(η^5-C_5H_5)] **3** 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 phenomena: (*a*) reversible co-ordination of [M(SC_6F_5)$_4$(η^5-C_5H_5)]$^-$ 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)$_4$(η^5-C_5H_5)] **3a** consists of a nine-line multiplet, δ −79.7, indicating that Cs$^+$ is co-ordinated by **1a** and coupled to eight equivalent *o*-fluorines, *J*(Cs–F) = 29.7 Hz (see Fig. 1). As the temperature is reduced the multiplet broadens, ultimately to give a quintet at −60 °C due to coupling to four equivalent *o*-fluorines, *J*(Cs–F) = 57.8 Hz. These data indicate that the SC_6F_5 groups adopt a fixed orientation at low temperature, as found in the solid state for Tl[Mo(SC_6F_5)$_4$(η^5-C_5H_5)], but that rotation/inversion of C_6F_5–S units occurs at higher temperatures, interchanging the two inequivalent



Scheme 1 (*i*) 3 Tl(SC_6F_5), CH_2Cl_2; (*ii*) excess of M′(SC_6F_5), thf; (*iii*) 5M′(SC_6F_5), thf

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† Typical experimental procedures, using Schlenk-type techniques: (*a*) [MoI$_3$(CO)$_2$(η^5-C_5H_5)] (0.25 g, 0.42 mmol) and Cs(SC_6F_5) (0.70 g, 2.1 mmol) in thf (40 cm^3), 6 h, room temperature (r.t.), produced **3a**, isolated after evaporation of solvent, extraction with diethyl ether, and recrystallisation from diethyl ether–light petroleum as red-orange crystals (10%). (*b*) [W(SC_6F_5)$_3$(CO)(η^5-C_5H_5)] (0.122 g, 0.14 mmol) and Cs(SC_6F_5) (0.093 g, 0.28 mmol) in thf (30 cm^3), 2 h, r.t., produced M′[W(SC_6F_5)$_4$(η^5-C_5H_5)] (M′ = Cs), isolated as above as yellow microcrystals (13%). Similar reactions yielded derivatives with M′ = Rb (39), K (29), Na·thf (63) or Li·4 thf (22%). All new compounds had satisfactory elemental analyses and ^{1}H and ^{19}F NMR spectra.

‡ Chemical shifts are to high frequency of CCl_3F (^{19}F, δ 0) and 0.1 mol dm^{-3} CsCl(aq) (^{133}Cs, δ 0).

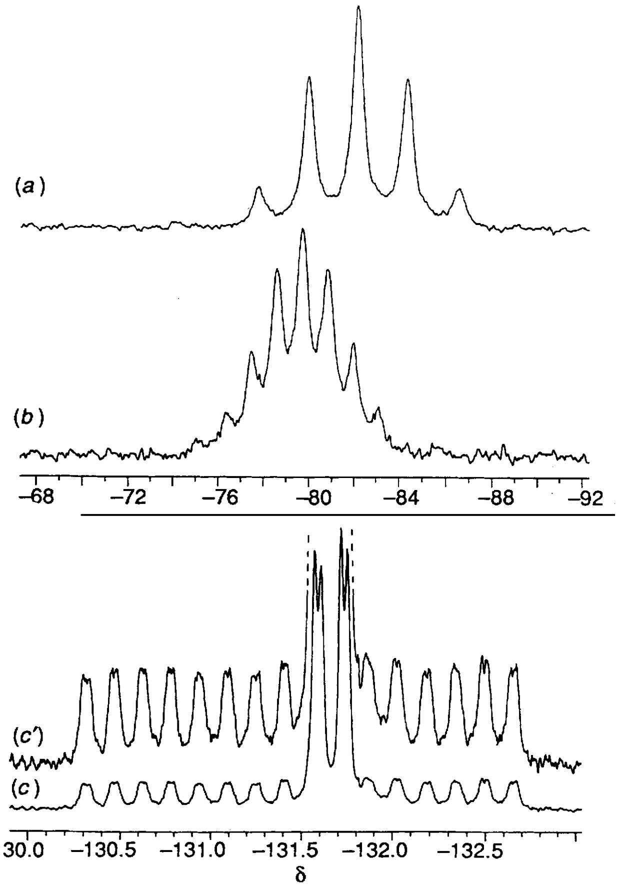

Fig. 1 The NMR spectra of Cs[Mo(SC_6F_5)$_4$(η^5-C_5H_5)] **3a**: (*a*) ^{133}Cs (−60 °C, $CD_3C_6D_5$), (*b*) ^{133}Cs (−20 °C, $CD_3C_6D_5$), (*c*) ^{19}F (−60 °C, CD_2Cl_2), C_6F_5 *o*-fluorine resonances and (*c'*) vertical expansion of (*c*)

fluorines and also the *m*-fluorines on each ring, without the loss of Cs^+. Corresponding changes in the ^{19}F NMR spectrum are observed over the range 18 to −80 °C. At 40 °C one set of broad *o*-, *m*- and *p*-fluorine resonances is present; coupling to $^{133}Cs^+$ ($I = \frac{7}{2}$, 100% abundant) as well as to other F atoms (principally *m*-fluorines) gives a complex multiplet for the *o*-fluorine resonance, which collapses to the predicted octet when the *m*-fluorines are decoupled. 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 a ring inequivalent. Only one of the *o*-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 there is also evidence for dissociation of Cs^+ at higher temperatures.

At 30 °C in CD_2Cl_2 the ^{133}Cs NMR spectrum of complex **3a** consists of a singlet, δ −15.1, consistent with non-interacting Cs^+ and [Mo(SC_6F_5)$_4$(η^5-C_5H_5)]$^-$ ions or with these ions undergoing a rapid exchange process. As the temperature is reduced the singlet broadens to give a quintet at −60 °C due to coupling to four equivalent *o*-fluorines, *J*(Cs–F) = 57.6 Hz, as above indicating co-ordination of the anion to Cs^+. In the ^{19}F NMR spectrum at room temperature no coupling to ^{133}Cs is observed and only one set of broad *o*-, *m*- and *p*-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. Moreover, one *o*-fluorine resonance is split into eight equal-intensity multiplets with well resolved coupling to ^{133}Cs, *J*(Cs–F) = 58.6 Hz (see Fig. 1).

That co-ordination of the caesium by anion **1a** and fluxional behaviour of the SC_6F_5 groups are independent processes is confirmed by the ^{19}F NMR spectra obtained in $(CD_3)_2CO$. At room temperature one set of *para*, *meta* and *ortho* resonances is observed but coupling to caesium is absent. However, although each of the latter two resonances is split into two inequivalent bands at −80 °C, *i.e.* the SC_6F_5 groups adopt a preferred orientation, coupling to ^{133}Cs is not observed, indicating that rigid co-ordination to Cs^+ has not occurred even at this temperature. We interpret this in terms of a greater solvation energy for caesium by $(CD_3)_2CO$ relative to CD_2Cl_2, an effect also observed with thallium(I).[1,2]

Variable-temperature ^{19}F NMR spectra of derivatives of K^+ and Rb^+ show similar features to those of complexes **3**, except for the absence of spin–spin coupling between ^{19}F and the cation in any of the solvent systems; this fact is not surprising in view of the higher nuclear quadrupole moment of these metals. Moreover, coalescence temperatures for *meta* and *ortho* resonances, and corresponding free energies of activation (*e.g.* in CD_2Cl_2: M = W, M' = Cs, Rb or K, $\Delta G_c^‡$ 50.9–52.3 ± 0.6 kJ mol^{-1}) for fluxionality of C_6F_5S groups, are all closely related for these larger alkali-metal derivatives and it may be inferred that complexation of Rb^+ and K^+ by anions **1** takes place. On the other hand, lower $\Delta G_c^‡$ values are found for the thf-solvated species (*e.g.* in CD_2Cl_2: M = W; M' = Na^+, $\Delta G_c^‡ = 46.6 \pm 0.5$ kJ mol^{-1}; M' = Li^+, $\Delta G_c^‡ = 41.3 \pm 0.8$ kJ mol^{-1}) suggesting that solvation prevents, or at least interferes with, co-ordination of these cations to the organometallic ligand.

Use of transition-metal complexes containing terminal thiolate ligands to co-ordinate other transition metals is well established[3] but co-ordination to alkali metals is, to our knowledge, unknown. It is also unexpected in view of the preference of alkali metals to co-ordinate with hard bases such as oxygen. As described earlier the thallium in Tl[Mo(SC_6F_5)$_4$(η^5-C_5H_5)] is co-ordinated primarily *via* the sulfurs, the interaction with four *o*-fluorines being primarily non-bonding. In contrast, the related Ru–SC_6F_4(F-2) chelate ring in [Ru{SC_6F_4(F-2)}(SC_6F_5)$_2$(PMe_2Ph)$_2$] contains a well defined Ru–F bond (2.489 Å).[4] It is therefore conceivable that in the alkali-metal derivatives described herein, the alkali-metal ion may prefer co-ordination to the *o*-fluorine atoms as hard donors rather than the soft sulfur atoms of the C_6F_5S groups. This question is not directly resolved by the NMR data which do not distinguish between the sulfur-co-ordinated structure with secondary weak interactions to fluorine, as in **3'**, and the alternative, principally fluorine-co-ordinated form of **3''** (see Scheme 1). However, it is noteworthy that fluorinated aromatic macrocycles in spherand ligands with complementary cavities for respective alkali-metal ions do not bind either Cs^+ or Li^+,[5] so that co-ordination by aromatic fluorine atoms is also novel. Ion pairing between alkali-metal salts of metal carbonyl anions is well known[6] but the M–CO–cation interaction appears to be much less directional and significantly weaker than the bonding reported herein.

Acknowledgements

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