Reactions of Monocyclopentadienyl Complexes of Molybdenum and Tungsten with Derivatives of Phenols and Pentafluorobenzeneselenol

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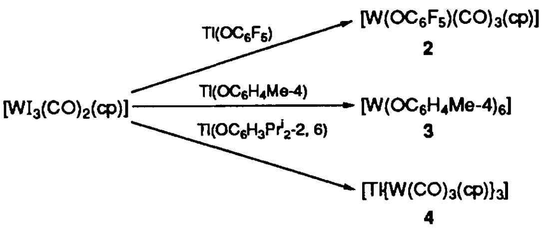
Reactions of [$\text{WI}_3(\text{CO})_2(\text{cp})$] (cp = η^5-C_5H_5) with thallium salts Tl(OR) (R = aryl) in tetrahydrofuran did not produce simple substitution products but afforded reduced species [$\text{W}(\text{OC}_6\text{F}_5)(\text{CO})_3(\text{cp})$] **2**, oxidised species [$\text{W}(\text{OC}_6\text{H}_4\text{Me}$-*p*$)_6$] or the thallium tritungsten derivative [$\text{Tl}\{\text{W}(\text{CO})_3(\text{cp})\}_3$] (when R = $\text{C}_6\text{H}_3\text{Pr}^i{}_2$-2,6). Complex **2** is a rare example of a derivative of type [$\text{WX}(\text{CO})_3(\text{cp})$] in which X is an oxygen-bonded ligand. Photolysis of [$\{\text{Mo}(\text{CO})_3(\text{cp})\}_2$] with $\text{Se}_2(\text{C}_6\text{F}_5)_2$ in toluene yields [$\text{Mo}(\text{SeC}_6\text{F}_5)(\text{CO})_3(\text{cp})$] **8a**, and the thermal reaction of [$\text{MoCl}(\text{CO})_3(\text{cp})$] with two equivalents of $\text{Tl}(\text{SeC}_6\text{F}_5)$ in diethyl ether gives the thallium complex $\text{Tl}[\text{Mo}(\text{SeC}_6\text{F}_5)_2(\text{CO})_2(\text{cp})]$ **9**, *via* complex **8a** isolated as a by-product. Reaction of [$\text{WBr}_3(\text{CO})_2(\text{cp})$] with three equivalents of $\text{Tl}(\text{SeC}_6\text{F}_5)$ produces [$\text{W}(\text{SeC}_6\text{F}_5)_3(\text{CO})(\text{cp})$] **12**, with [$\text{W}(\text{SeC}_6\text{F}_5)(\text{CO})_3(\text{cp})$] **8b** as a by-product, and further reaction of **12** with $\text{Tl}(\text{SeC}_6\text{F}_5)$ forms [$\text{TlW}(\text{SeC}_6\text{F}_5)_4(\text{cp})$] **11b**. Variable-temperature ^{19}F NMR studies show that complexes **9**, **11b** and **12** are fluxional and show hindered motion of the C_6F_5 rings. In complexes **9** and **11b**, thallium(I) is co-ordinated by the selenolate ligands of the organometallic anion and coupling between $^{103/105}$Tl and ^{19}F *ortho*-fluorine nuclei is observed in the ^{19}F NMR spectra. Complex **12** comprises two conformers in equilibrium which are detected by NMR studies at low temperature. Comparisons are drawn between properties of the new selenium complexes and related sulfur derivatives.

Previously we have described the chemistry of cyclopentadienyl molybdenum-(II) and -(IV) and tungsten(IV) complexes with pentafluorobenzenethiolate ligands.[1-3] These complexes include the thallium derivatives $\text{Tl}[\text{Mo}(\text{SC}_6\text{F}_5)_2(\text{CO})_2(\text{cp})]$ (cp = η^5-C_5H_5) and [$\text{TlM}(\text{SC}_6\text{F}_5)_4(\text{cp})$] (M = Mo or W) in which the thallium(I) ion reversibly co-ordinates to the sulfur atoms of the organometallic anion and, in the latter species, occupies a cavity formed by the transition metal, the four sulfurs and four *ortho*-fluorines of the pentafluorophenyl rings. Interactions between thallium and *ortho*-fluorine atoms are observable by NMR spectroscopy in solution[1,2] and similar co-ordination of larger alkali-metal metal ions such as caesium also occurs.[3] These findings have possible implications in the development of organometallic ligands as sequestration agents or as metal-ion sensors. In this paper we report an extension of these studies to include oxygen- or selenium-containing ligands which should provide products with differing geometric and electronic features for potential applications as new organometallic ligands.

Results and Discussion

Reactions with Thallium Phenolates.—Since reactions of the complexes [$\text{MX}_3(\text{CO})_2(\text{cp})$] (M = Mo or W; X = Cl, Br or I) with >4 equivalents of $\text{Tl}(\text{SC}_6\text{F}_5)$ give the well characterised species [$\text{TlM}(\text{SC}_6\text{F}_5)_4(\text{cp})$] (M = Mo **1a** or W **1b**) in $>30\%$ yield,[2] similar reactions of Group 6 metal complexes with phenolates TlOR (R = aryl) have been investigated. Monitoring of the reaction between [$\text{WI}_3(\text{CO})_2(\text{cp})$] and excess $\text{Tl}(\text{OC}_6\text{F}_5)$ in tetrahydrofuran (thf) by IR spectroscopy indicated completion after 6 d at ambient temperature, but work-up afforded red crystals of the tungsten(II) derivative [$\text{W}(\text{OC}_6\text{F}_5)(\text{CO})_3(\text{cp})$] **2** as the only isolable pure product, obtained in low yield (Scheme 1). Other products included uncharacterised species, formed by loss of the cyclopentadienyl ligand. IR studies of similar reactions between [$\text{MoCl}_2(\eta^3$-$\text{C}_3\text{H}_5)(\text{CO})(\text{cp})$] and $\text{Tl}(\text{OC}_6\text{F}_5)$ supported the formation of the molybdenum analogue of **2**, *i.e.* [$\text{Mo}(\text{OC}_6\text{F}_5)(\text{CO})_3(\text{cp})$], in solution but only impure, non-cyclopentadienyl molybdenum species and free pentafluorophenol could be isolated as products.



Scheme 1

Although tricarbonyl(η^5-cyclopentadienyl)tungsten(II) complexes of general formula [$\text{WX}(\text{CO})_3(\text{cp})$] are well known, such complexes in which X is an oxygen ligand are rare and complex **2** is a new, characterised example. The structure is supported by analytical data, IR, MS, ^{1}H and ^{19}F NMR spectra. The ^{19}F NMR spectrum of complex **2** is typical of a compound with a symmetrical C_6F_5 group and there is no evidence from variable-temperature studies down to -80 °C in [$^2\text{H}_8$]toluene solutions for restricted rotation of this group. It is of interest that non-isolable, paramagnetic complexes formed in solution by photolysis of [$\{\text{Mo}(\text{CO})_3(\text{cp})\}_2$] with 1,4-benzoquinones have been assigned a related structure to **2** with a benzoquinone radical as an oxygen-bound ligand, [$\text{Mo}(\text{ORO}^\bullet$-4$)(\text{CO})_3(\text{cp})$] (R = C_6H_4 or substituted *para*-phenylene unit, including C_6F_4), and there is evidence from the lowest temperature ESR studies (-90 °C) for some restriction in motion about the C–O(–Mo) bond of the generally, freely rotating benzoquinone ligands.[4] It should be noted that the shorter time-scale of ESR would reveal exchanges with lower energy barriers than NMR spectroscopy.

Reactions of [$\text{WI}_3(\text{CO})_2(\text{cp})$] with 4–6 equivalents of $\text{Tl}(\text{OC}_6\text{H}_4\text{Me}-4)$ in thf over 5–6 d at ambient temperature produce [$\text{W}(\text{OC}_6\text{H}_4\text{Me}-4)_6$] **3** as the principal product, isolated in *ca.* 50% yield (Scheme 1). This and related hexaphenolatotungsten(VI) compounds have been prepared previously from $WOCl_4$.[5] The formation of **3** from $[WI_3(CO)_2(cp)]$ is unexpected and involves oxidation and complete ligand substitution of the organometallic precursor. From a related reaction of $[WI_3(CO)_2(cp)]$ with the bulky, *ortho*-disubstituted phenolate, $Tl(OC_6H_3Pr^i_2\text{-}2,6)$, the only pure crystalline product, isolable in low yield, was the known[6] thallium tritungsten complex, $[Tl\{W(CO)_3(cp)\}_3]$ **4**. The IR spectra taken during an analogous reaction of $Tl(OC_6H_4OMe\text{-}2)$ with $[WI_3(CO)_2(cp)]$ indicated a similar reaction course, with complex **4** being formed in solution but only an impure orange material could be isolated as a solid product.

Reactions of Pentafluorobenzeneselenol Derivatives.—Tricarbonyl(η^5-cyclopentadienyl)molybdenum halides, $[MoX(CO)_3(cp)]$, react with $Tl(SC_6F_5)$ to produce $Tl[Mo(SC_6F_5)_2(CO)_2(cp)]$ **5**, which can be converted oxidatively in a thermal reaction with further $Tl(SC_6F_5)$ or in a photochemical reaction with $S_2(C_6F_5)_2$ into $[TlMo(SC_6F_5)_4(cp)]$ **1a**;[1,3] the simple molybdenum thiolate $[Mo(SC_6F_5)(CO)_3(cp)]$ **6a** is a precursor in the initial preparation of complex **5**. Tungsten does not form a compound of type **5**, although the simple thiolate $[W(SC_6F_5)(CO)_3(cp)]$ **6b** can be synthesised and photochemical reaction of this complex with $Tl(SC_6F_5)$ does produce $[TlW(SC_6F_5)_4(cp)]$ **1b** but only in small amounts and the latter species is best synthesised from tungsten(IV) complexes $[WX_3(CO)_2(cp)]$ *via* the isolable intermediate $[W(SC_6F_5)_3(CO)(cp)]$ **7**.[2,3] Related reactions using $Tl(SeC_6F_5)$ or $Se_2(C_6F_5)_2$[7,8] as reagents were studied in this work in attempts to prepare selenium analogues of the sulfur compounds **1** and **5**–**7**.

Compound $[Mo(SeC_6F_5)(CO)_3(cp)]$ **8a** is formed by photolysis of $Se_2(C_6F_5)_2$ with $[\{Mo(CO)_3(cp)\}_2]$, equation (1). Related selenium complexes, including $[Mo(SeC_6H_5)(CO)_3(cp)]$,[9] have been previously reported and the new complex **8a** shows a similar IR spectrum. Although $[Mo(SeC_6H_5)(CO)_3(cp)]$ is unstable in solution and is transformed into dinuclear $[\{Mo(SeC_6H_5)(CO)_2(cp)\}_2]$,[9] the mononuclear complex **8a** is stable, as is the corresponding pentafluorobenzenethiolate complex **6a**, and this stability may be attributed to the presence of the electron-withdrawing C_6F_5 group. Variable-temperature ^{19}F NMR spectra of **8a** show no evidence for restricted rotation of the single C_6F_5 group and the ^{77}Se NMR resonance is a well defined triplet, showing coupling with *ortho*-F atoms [J(F-Se) 24.5 Hz].

$$[\{Mo(CO)_3(cp)\}_2] \xrightarrow[h\nu/\text{toluene}]{Se_2(C_6F_5)_2} [Mo(SeC_6F_5)(CO)_3(cp)] \quad (1)$$

8a

Reaction of $[MoCl(CO)_3(cp)]$ with two equivalents of $Tl(SeC_6F_5)$, equation (2), affords the thallium derivative

$$[MoCl(CO)_3(cp)] \xrightarrow[Et_2O]{Tl(SeC_6F_5)} Tl[Mo(SeC_6F_5)_2(CO)_2(cp)] \quad (2)$$

9

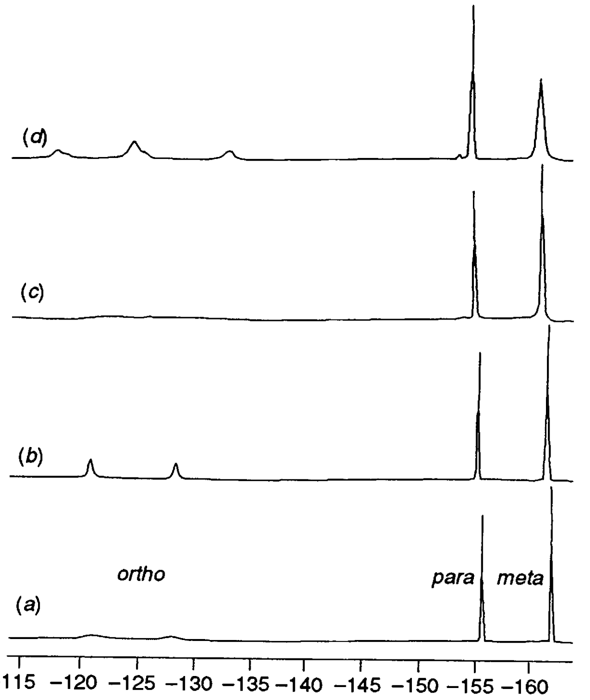
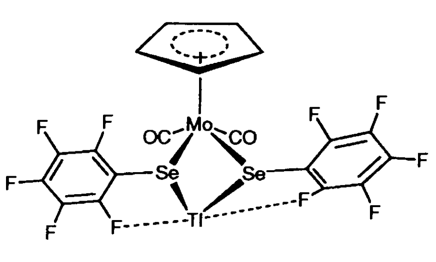


Fig. 1 ^{19}F NMR spectra of $Tl[Mo(SeC_6F_5)_2(CO)_2(cp)]$ **9** in CD_2Cl_2 solution at (*a*) +18, (*b*) −20, (*c*) −80 and (*d*) −95 °C



9

$Tl[Mo(SeC_6F_5)_2(CO)_2(cp)]$ **9**, formed *via* the monoselenolate **8a** which is removed as a by-product. Spectroscopic properties of complex **9** indicate that it is related to $Tl[Mo(SC_6F_5)_2(CO)_2(cp)]$ **5** and variable-temperature NMR studies can be rationalised in terms of a similar structure.[1] The ^{19}F NMR spectra of **9** in CD_2Cl_2 solution at various temperatures are depicted in Fig. 1. The doublet resonance [J(Tl-F) 1310 Hz] at ambient temperatures, with broad components and assignable to four equivalent *ortho*-F atoms, initially sharpens on cooling and then passes through a coalescence point at *ca.* −80 °C to become, at −95 °C, a broadened doublet resonance [J(Tl-F) 2805 Hz] and a broad single resonance, each signal assignable to two *ortho*-F atoms. At the lowest temperature Tl^+ ($^{203/205}Tl$, $I = 0.5$) interacts with two *ortho*-F atoms producing the large doublet splitting and interchange of *ortho*-F atoms by rotation (or inversion/rotation) of the C_6F_5 groups is slow so that the two sets of *ortho*-F atoms are inequivalent and only one of the two resonances is a doublet; at higher temperatures the rate of interchange of *ortho*-F atoms is fast on the NMR time-scale but co-ordination of Tl^+ persists and a doublet with a coupling constant of approximately half the magnitude is observed; at ambient temperatures the broadening of this resonance is assigned to some dissociation of co-ordinated thallium(I), equation (3). In the rigid structure, both *meta*-F atoms should

$$Tl[Mo(SeC_6F_5)_2(CO)_2(cp)] \rightleftharpoons Tl^+ + [Mo(SeC_6F_5)_2(CO)_2(cp)]^- \quad (3)$$

also be inequivalent but the broadened resonance at −95 °C indicates that the rate of rotation of the C_6F_5 systems is still significant in terms of the frequency difference between resonances of these atoms. Interestingly, in CD_2Cl_2 solution the sulfur analogue **5** shows more evidence for ionic dissociation of the Tl^+ ion since the *ortho*-F resonance is a broad singlet at 20 °C and, although a doublet [J(Tl-F) 1800 Hz] is observed at lower temperatures, the sulfur species appears to be less rigid since this band is not resolved into two separate resonances at −90 °C.[1] Only in the less polar medium $C_6D_5CD_3$–Et_2O (1 : 1), at 100 °C, are separate resonances resolved for the two sets of *ortho*-fluorine atoms of complex **5** and the coupling constant, J(Tl–F) 3770 Hz, in this rigid form is significantly larger than that of 2805 Hz for complex **9**.

The reaction of $[Mo(SC_6F_5)(CO)_3(cp)]$ with $Tl(SeC_6F_5)$, equation (4), does provide the mixed species $Tl[Mo(SC_6F_5)$-

$$[\mathrm{Mo(CO)_3(SC_6F_5)(cp)}] \xrightarrow[\mathrm{Et_2O}]{\mathrm{Tl(SeC_6F_5)}} \underset{\mathbf{10}}{\mathrm{Tl[Mo(SC_6F_5)(SeC_6F_5)(CO)_2(cp)]}} + \underset{\mathbf{5}}{\mathrm{Tl[Mo(SC_6F_5)_2(CO)_2(cp)]}} + \underset{\mathbf{9}}{\mathrm{Tl[Mo(SeC_6F_5)_2(CO)_2(cp)]}} \quad (4)$$

$(SeC_6F_5)(CO)_2(cp)]$ **10** as a major product. However, some redistribution of chalcogen ligands occurs so that complexes **5** and **9** are also formed. One sample isolated after crystallisation of the reaction products contained S > Se, as shown by elemental composition and analysis of the ^{19}F NMR spectrum, with an average formula $Tl[Mo(SC_6F_5)_{1.2}(SeC_6F_5)_{0.8}(CO)_2(cp)]$, (see Experimental section), but other crystalline samples were selenium rich, and these results were consistent with the formation of a mixture of the three species $Tl[Mo(SC_6F_5)_x(SeC_6F_5)_{2-x}(CO)_2(cp)]$ (x = 0, 1 or 2).

Unlike the corresponding sulfur complex **1a**, the molybdenum(IV) derivative $[TlMo(SeC_6F_5)_4(cp)]$ **11a** could not be obtained as a pure product from reactions of $[MoCl_3(CO)_2(cp)]$ and $Tl(SeC_6F_5)$: two complexes formed in this reaction were complexes **8a** and **9**, identified by IR spectroscopy, whilst isolated products were $Se_2(C_6F_5)_2$ and a mixture of other η^5-cyclopentadienylmolybdenum products probably including complex **11a**. Other attempts to prepare cyclopentadienylmolybdenum(IV) selenolate complexes from molybdenum(II) precursors were also unsuccessful. On the other hand, characterised tungsten(IV) derivatives, $[W(SeC_6F_5)_3(CO)(cp)]$ **12** and $[TlW(SeC_6F_5)_4(cp)]$ **11b**, were synthesised by methods similar to those employed for the analogous thiolate species, equations (5) and (6).

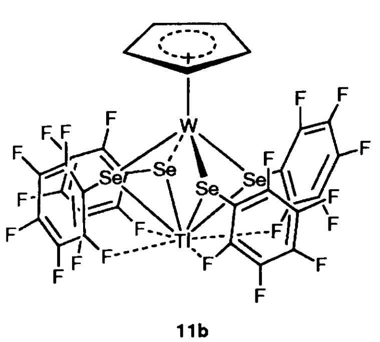
$$[\mathrm{WBr_3(CO)_2(cp)}] \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{Tl(SeC_6F_5)}} \underset{\mathbf{12}}{[\mathrm{W(SeC_6F_5)_3(CO)(cp)}]} + \underset{\mathbf{8b}}{[\mathrm{W(SeC_6F_5)(CO)_3(cp)}]} \quad (5)$$

$$[\mathrm{W(CO)(SeC_6F_5)_3(cp)}] \xrightarrow[\mathrm{thf}]{\mathrm{Tl(SeC_6F_5)}} \underset{\mathbf{11b}}{[\mathrm{TlW(SeC_6F_5)_4(cp)}]} \quad (6)$$

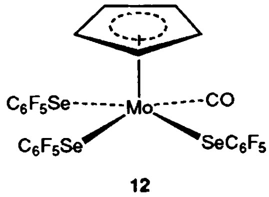
Compound $[W(SeC_6F_5)_3(CO)(cp)]$ **12** was obtained in 46% yield as dark, needle-like crystals from the reaction of $[WBr_3(CO)_2(cp)]$ with 3 equivalents of $Tl(SeC_6F_5)$ in dichloromethane. A by-product of this reaction was the reduced species $[W(SeC_6F_5)(CO)_3(cp)]$ **8b**, isolated in only 1.3% yield, and characterised by IR, ^{19}F and ^1H NMR spectra, by the EI mass spectrum which contained a prominent molecular ion and characteristic fragmentation ions, and by comparison with the molybdenum analogue **8a**. The $Tl(SeC_6F_5)$ displaces CO from $[W(SeC_6F_5)_3(CO)(cp)]$ **12** in tetrahydrofuran solution and red microcrystals of $[TlW(SeC_6F_5)_4(cp)]$ **11b** can be isolated from the reaction mixture in 8.5% yield.

Characterisation of $[W(SeC_6F_5)_3(CO)(cp)]$ **12** was based on elemental analysis, the single ν(CO) band at 2013 cm^{-1} in the IR spectrum, a singlet resonance in the ^1H NMR spectrum, and on variable-temperature ^{19}F NMR spectra: a 'piano-stool' structure related to that determined by X-ray diffraction for the sulfur derivative **7** is consistent with these results. The resonances in the ambient-temperature ^{19}F NMR spectrum are assignable to two equivalent C_6F_5Se ligands *cis* to CO and to one C_6F_5Se ligand *trans* to CO, with rapid rotation (or rotation/inversion) about the C_6F_5–Se–W bonds causing the symmetrical patterns for these two sets of C_6F_5 resonances. At lower temperatures, barriers to motion of the *cis*-C_6F_5Se ligands cause slower interchange between conformational isomers on the NMR time-scale and at −100 °C the presence of two forms is evident. Analysis of the data supports conformation **B** for the major species with both *cis*-C_6F_5 ligands oriented towards the less bulky CO ligand and with hindered rotation of these ligands causing the two *ortho*- and two *meta*-fluorine environments of each ring to be inequivalent. The less hindered *trans*-C_6F_5Se ligand, however, is undergoing rapid rotation (or rotation/inversion) and this creates an apparent plane of symmetry in the complex. Thus, isomer **B** exhibits three *ortho*-fluorine resonances of equal intensities and two triplet *para*-fluorine resonances of relative intensities 2 : 1 (see Fig. 2). The minor isomer observed at low temperatures in solution probably has conformation A, related to that of complex **7** in the solid state, with three inequivalent C_6F_5Se ligands, each giving separate *para*-fluorine triplet resonances of equal intensities [see Fig. 2(*d*)].

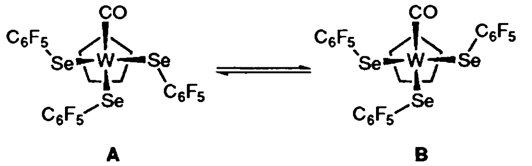
Compound $[TlW(SeC_6F_5)_4(cp)]$ **11b** shows similar spectroscopic properties to those of the tetrathiolate complex **1b**. The ^{19}F NMR spectra indicate that coupling between *ortho*-fluorine and $^{203/205}Tl$ nuclei occurs, supporting the placement of Tl^+ within a cavity formed by the four selenolate ligands and the tungsten atom, as illustrated. At −60 °C or below in CD_2Cl_2 the ^{19}F NMR spectrum of complex **11b** is consistent with this rigid structure: the resonance of four *ortho*-fluorine atoms includes a large doublet splitting, J(Tl–F) 2528 Hz, whereas the opposite four *ortho*-fluorine atoms on each ring show no significant coupling to $^{203/205}Tl$, and the two sets of *meta*-fluorine atoms show different chemical shifts. At higher temperature the rate of C_6F_5 rotation increases and the *meta*- and *ortho*-fluorine atoms become equivalent; at ambient



11b



12



A **B**

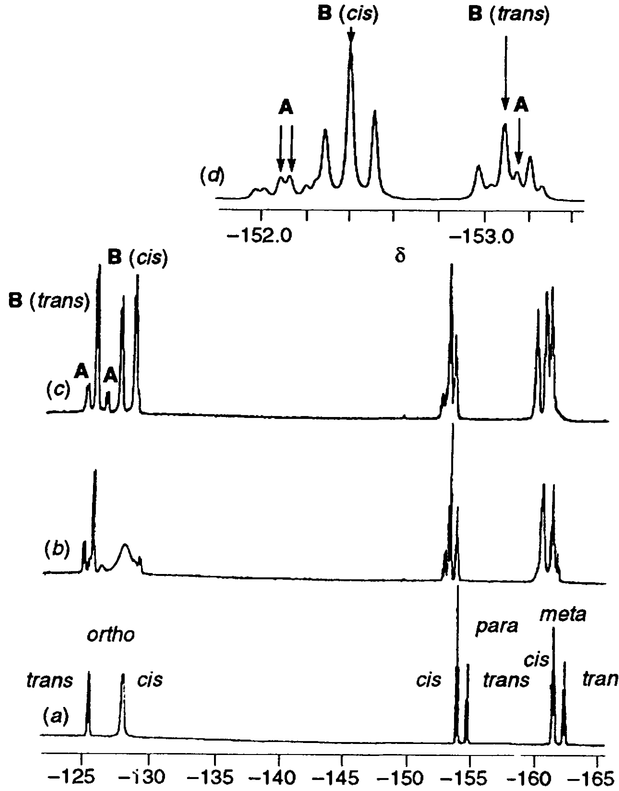


Fig. 2 ^{19}F NMR spectra of $[W(SeC_6F_5)_3(CO)(cp)]$ **12**: (*a*) +20 °C in CD_2Cl_2–Et_2O; (*b*) −20 °C in CD_2Cl_2–Et_2O; (*c*) −100 °C in CD_2Cl_2–Et_2O; (*d*) expansion of *para*-fluorine triplet resonances at −80 °C in CD_2Cl_2. Assignments are given for *cis*- and *trans*-C_6F_5Se ligands and for conformers **A** and **B** (see text)

temperatures the *meta*-fluorine resonance is in the fast-exchange regime, *via* coalescence at −20 °C, whereas residual broadening of the *ortho*-fluorine doublet, with J(Tl–F) ≈ 1300 Hz, is attributable to an intermediate exchange rate with respect to the energy difference between the resonances of the atoms (see Fig. 3). In $[^2H_8]$toluene solution, similar ^{19}F NMR spectra are observed and at +40 °C the components of the doublet (J 1312 Hz) are sharper due to faster exchange of *ortho*-fluorine atoms. It should be noted that throughout these temperature ranges in CD_2Cl_2 or $C_6D_5CD_3$ solutions the coupling to thallium is retained so that Tl^+ remains associated with the anion $[W(SeC_6F_5)_4(cp)]^-$ even though the C_6F_5Se groups are fluxional. The free energy of activation, $\Delta G^‡$, calculated for the fluxional process of complex **11b** at the coalescence of *meta*-fluorine resonances in CD_2Cl_2 is 47.7 ± 1.0 kJ mol^{-1} and this is marginally higher than the value of 46.7 ± 1.0 kJ mol^{-1} for the thiolate analogue **1b**. It should be noted that the coupling between Tl^I and the four *ortho*-fluorine atoms in the rigid form of the sulfur complex **1b** [J(Tl–F) 3537 Hz at −80 °C in CD_2Cl_2][2] is significantly larger than in derivative **11b** and this difference is probably a consequence of the geometry of the cavity with the Tl–Se bonding in the selenolate complex causing longer Tl–F distances. The bonding interaction between thallium and fluorine atoms is believed to be minimal in these complexes.

Conclusions

It appears that oxygen analogues of the sulfur species $[TlM(SC_6F_5)_4(cp)]$ **1** cannot be readily prepared from reactions of thallium phenolates with η^5-cyclopentadienylmetal(IV) reagents. The products obtained from reactions $[WI_3(CO)_2(cp)]$ (see Scheme 1) include reduced tricarbonyl(η^5-cyclopentadienyl)tungsten(II) species, and there is IR spectral evidence for the formation of such species during the course of all reactions. In some reactions oxidised hexaphenolatotungsten(VI) compounds are the final products, formed *via* cleavage of all C-bonded ligands.

The selenolate complexes **8**, **9**, **11** and **12** analogous to the known sulfur species $[M(SC_6F_5)(CO)_3(cp)]$ **6** (M = Mo or W), $Tl[Mo(SC_6F_5)_2(CO)_2(cp)]$ **5**, $[TlW(SC_6F_5)_4(cp)]$ **1b** and $[W(SC_6F_5)_3(CO)(cp)]$ **7**, respectively, can be synthesised. In the thallium derivatives **9** and **11** the observation of thallium–fluorine coupling in ^{19}F NMR spectra supports the co-ordination of Tl^+ by the organometallic anion, most probably by a primary interaction with the selenium atoms with the co-ordination geometry leading to smaller values of coupling constants J(Tl–F) than in the sulfur derivatives **5** and **1b**. The sulfur and selenium complexes show similar fluxionality of C_6F_5 groups and tendency to dissociation of the Tl^+ ions, although the selenium species appear to be slightly more rigid and less ionically dissociated than sulfur analogues under comparable conditions. These studies show that organometallic selenolate anions such as $[W(SeC_6F_5)_4(cp)]^-$ act as polydentate ligands for Tl^+ and may have potential for complexing other metal ions.

Experimental

All reactions and manipulations were carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were purified and dried as previously described, and light petroleum had a boiling point range of 60–80 °C. The starting materials $[\{M(CO)_3(cp)\}_2]$,[10] $[MCl(CO)_3(cp)]$,[10] $[MX_3(CO)_2(cp)]$[11] (M = Mo or W; X = Cl, Br or I), $[Mo(SC_6F_5)(CO)_3(cp)]$[12] and $Tl[Mo(SC_6F_5)_2(CO)_2(cp)]$[1] were synthesised by literature methods. Thallium salts, Tl(OR) (R = C_6F_5, 4-MeC_6H_4 or 2,6-$Pr^i{}_2C_6H_3$), were prepared from thallium(I) acetate and the appropriate phenol in methanol by precipitation after addition of aqueous KOH. Compounds $M(CO)_6$ (M = Mo or W), pentafluorobenzenethiol, pentafluorophenol, *p*-cresol, 2,6-diisopropylphenol, bromopentafluorobenzene, thallium(I) acetate and selenium powder were obtained commercially (BDH or Aldrich) and used as supplied. The ^1H, ^{19}F, ^{31}P and ^{77}Se NMR spectra were recorded on a Bruker WP 200 SY instrument at 200.13, 188.31, 80.32 and 38.17 MHz, respectively, using $SiMe_4$, CCl_3F, 85% aqueous H_3PO_4 and Me_2Se as references (δ 0.0) with positive shifts (ppm) to high frequency, at *ca.* 20 °C unless otherwise stated. The ^{19}F NMR spectra were also recorded at 75.40 MHz on a Bruker WP 80 instrument. The IR spectra were recorded on a Perkin-Elmer FT1600 spectrometer in dichloromethane solution, unless otherwise stated, and EI mass spectra (MS) were obtained on an upgraded VG MS9 instrument. Elemental analyses were carried out at UMIST, Manchester.

Reaction of $[WI_3(CO)_2(cp)]$ *with* $Tl(OC_6F_5)$.—The compounds $[WI_3(CO)_2(cp)]$ (0.374 g, 0.55 mmol) and $Tl(OC_6F_5)$ (1.33 g, 3.4 mmol) were stirred at ambient temperature in tetrahydrofuran (60 cm^3) for 6 d. The solvent was removed under vacuum and the residue extracted with diethyl ether (40 cm^3). The solution was filtered, reduced in volume and cooled at −15 °C to give red crystals contaminated with much orange powder; separation of the crystals by hand afforded $[W(OC_6F_5)(CO)_3(cp)]$ **2**, 0.008 g (3%) (Found: C, 33.7; H, 1.1. $C_{14}H_5F_5O_4TlW$ requires C, 32.6; H, 1.0%). IR: ν(CO) 2048, 1962 and 1940 cm^{-1}. NMR ($C_6D_5CD_3$): ^1H, δ 4.73 (s C_5H_5); ^{19}F δ −161.7 (m, 2 *o*-F), −167.0 (m, 2 *m*-F) and −173.7 (tt, 6.95, 22.6, 1 *p*-F). MS, *m/z* (%, ^{184}W): 488 [18, $(M - CO)^+$], 460 [26, $(M - 2CO)^+$], 431 [34, $(M - 3CO)^+$], 184 (100, W^+); other ions include fragments of the molecule, and low-intensity peaks assigned to ditungsten ions, including 610 {4, $[W_2(CO)_4(cp)_2]^+$}.

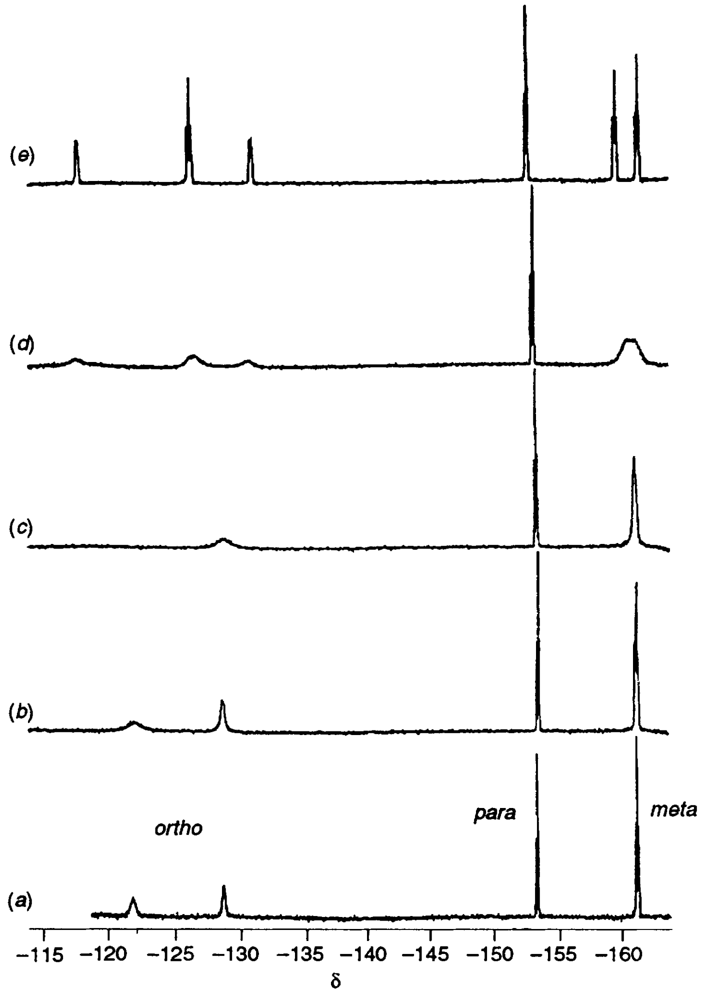


Fig. 3 ^{19}F NMR spectra of $[TlW(SeC_6F_5)_4(cp)]$ **11b**: (*a*) +40 °C in $[^2H_8]$toluene; (*b*) +19 °C in CD_2Cl_2; (*c*) 0 °C in CD_2Cl_2; (*d*) −20 °C in CD_2Cl_2; (*e*) −60 °C in CD_2Cl_2

Reaction of $[WI_3(CO)_2(cp)]$ *with* $Tl(OC_6H_4Me\text{-}4)$.—The compounds $[WI_3(CO)_2(cp)]$ (0.258 g, 0.38 mmol) and $Tl(OC_6H_4Me\text{-}4)$ (0.71 g, 2.3 mmol) were stirred at ambient temperature in tetrahydrofuran (60 cm^3) for 6 d. The solvent was removed under vacuum and the residue extracted with diethyl ether (40 cm^3). The solution was filtered, the filtrate reduced in volume and cooled at −15 °C to give dark red octahedral crystals of $[W(OC_6H_4Me\text{-}4)_6]$ **3** which were washed with light petroleum ether and dried *in vacuo*, yield 0.143 g (46%), m.p. 132–134 °C (lit.[5] 130–131 °C) (Found: C, 61.2; H, 5.35. $C_{42}H_{42}O_6W$ requires C, 61.0; H, 5.1%).

Reaction of $[WI_3(CO)_2(cp)]$ *with* $Tl(OC_6H_3Pr^i_2\text{-}2,6)$.—The compounds $[WI_3(CO)_2(cp)]$ (0.407 g, 0.59 mmol) and $Tl(OC_6H_3Pr^i_2\text{-}2,6)$ (1.439 g, 3.6 mmol) were stirred at ambient temperature in tetrahydrofuran (60 cm^3) for 6 d. The solvent was removed under vacuum and the residue extracted with diethyl ether (40 cm^3). After filtering and reduction in volume of the red extract, light petroleum was added and the solution cooled to −15 °C. Red crystals of $[Tl\{W(CO)_3(cp)\}_3]$ **4** separated and were collected, washed with light petroleum and dried *in vacuo*, 0.034 g (14%) (Found: C, 24.3; H, 1.3. $C_{24}H_{15}O_9TlW_3$ requires C, 23.9; H, 1.2%). IR (KBr): ν(CO) 1963, 1946, 1894 (sh) and 1880 cm^{-1}. NMR (C_6D_6): ^1H, δ 5.02 [d, *J*(Tl–H) 7.5 Hz, C_5H_5].

Preparation of C_6F_5SeH (cf. *ref.* 13) *and* $Se_2(C_6F_5)_2$ (cf. *ref.* 7).—Grignard reagent, pentafluorophenylmagnesium bromide, was prepared from bromopentafluorobenzene (61.7 g, 0.25 mol) and an equivalent amount of ethylmagnesium bromide in tetrahydrofuran (200 cm^3), according to the literature method.[14] To prevent formation of C_6F_5SeEt in the next step, the bromoethane by-product was removed by evaporation of the solution under vacuum and the total volume of the solution was subsequently made up to the original 200 cm^3 by more tetrahydrofuran. The resulting solution of $Mg(C_6F_5)Br$ was warmed to 40 °C and dry powdered black selenium (19 g, 0.24 mol) was added over a period of 30 min. Stirring was continued for a further 1 h. The contents of the flask were poured upon 400 g of crushed ice and with hand stirring concentrated hydrochloric acid (40 cm^3) was added. The cold mixture was filtered through glass-wool. The aqueous layer was separated and extracted with diethyl ether (5 × 200 cm^3). The combined extracts and main product were dried over calcium chloride. The ether was removed by distillation to leave pentafluorobenzeneselenol of adequate purity for further use. NMR (C_6D_6): ^{19}F, δ −130.7 (m, 2 *o*-F), −157.6 (t, 21.0, 1 *p*-F), −161.6 (m, 2 *m*-F); ^{77}Se, δ −43.1 (br). Bromine (1.0 g) was added dropwise to a stirred solution of pentafluorobenzeneselenol (1.50 g, 6.1 mmol) in acetic acid (15 cm^3). After 2 h the acetic acid was removed on a rotary evaporator. Vacuum sublimation of the oil gave yellow-orange crystals of $Se_2(C_6F_5)_2$[7,8] (0.95 g, 63%). NMR ($CDCl_3$): ^{19}F, δ −125.35 (m, 4 *o*-F), −148.8 (m, 2 *p*-F), −159.5 (m, 4 *m*-F); ^{77}Se, δ −372.3 (t, 20.3).

Preparation of $Tl(SeC_6F_5)$.—To a solution of thallium(I) acetate (3.00 g, 11.4 mmol) in methanol (80 cm^3) was added dropwise with stirring an excess of pentafluorobenzeneselenol. A yellow precipitate formed immediately. The solution was stirred for 10 min, cooled to 0 °C and the yellow product filtered off, washed with diethyl ether and then dried *in vacuo* (3.59 g, 70%). NMR [$(CD_3)_2CO$]: ^{19}F, δ −126.3 (br d, 23.4, 2 *o*-F), −163.3 (t, 19.5 Hz, 1 *p*-F) and −164.7 (m, 2 *m*-F).

Preparation of [$Mo(SeC_6F_5)(CO)_3(cp)$] **8a**.—The compounds [{$Mo(CO)_3(cp)$}$_2$] (530 mg, 1.08 mmol) and $(SeC_6F_5)_2$ (391 mg, 0.80 mmol) were photolysed in toluene (60 cm^3) with a medium pressure mercury lamp for 18 h (*cf.* ref. 15). 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-red crystals of **8a** (490 mg, 63%) (Found: C, 34.6; H, 1.2. $C_{14}H_5F_5MoO_3Se$ requires C, 34.2; H, 1.0%). NMR ($CDCl_3$): ^1H, δ 5.64 (s, C_5H_5); ^{19}F, δ −124.7 (dd, 27.7, 8.1, 2 *o*-F), −155.15 (t, 20.8, 1 *p*-F), −162.1 (m, 27.7, 20.8, 2 *m*-F); ^{77}Se, δ −385.3 (t, 24.5 Hz). IR: ν(CO) 2030 and 1948 cm^{-1}.

Preparation of Tl[$Mo(SeC_6F_5)_2(CO)_2(cp)$] **9**.—The compounds [$MoCl(CO)_3(cp)$] (507 mg, 1.81 mmol) and $Tl(SeC_6F_5)$ (1629 mg, 3.62 mmol) were stirred in diethyl ether (40 cm^3) for 4 d. The solution was filtered, centrifuged and pumped to dryness *in vacuo*. Washing with light petroleum removed unwanted [$Mo(SeC_6F_5)(CO)_3(cp)$] **8a**. Recrystallisation from dichloromethane–light petroleum afforded red crystals of **9** (338 mg, 20%) (Found: C, 24.7; H, 0.6. $C_{19}H_5F_{10}MoO_2Se_2Tl$ requires C, 25.0; H, 0.6%). NMR (CD_2Cl_2): ^1H, δ 5.70 (s, C_5H_5); ^{19}F (18 °C), δ −124.5 [br d, *J*(Tl–F) 1310, 4 *o*-F], −155.8 (t, 21.0, 2 *p*-F), −162.1 (m, 4 *m*-F); ^{19}F (−95 °C) δ −124.5 (br s, 2 *o*-F), −125.45 [br d, *J*(Tl–F) 2805, 2 *o*-F), −154.9 (t, 21.8 Hz, 2 *p*-F), −161.0 (br s, 4 *m*-F). IR: ν(CO) 1951 and 1872 cm^{-1}.

Reaction of [$Mo(SC_6F_5)(CO)_3(cp)$] *with* $Tl(SeC_6F_5)$.—The compounds [$Mo(SC_6F_5)(CO)_3(cp)$] (447 mg, 1.01 mmol) and $Tl(SeC_6F_5)$ (455 mg, 1.01 mmol) were stirred together in diethyl ether (40 cm^3) for 2 d. The solution was filtered, centrifuged and pumped to dryness *in vacuo*. Washing with light petroleum removed unreacted [$Mo(SC_6F_5)(CO)_3(cp)$]. Recrystallisation from dichloromethane–light petroleum afforded dark red crystals (189 mg). [Found: C, 26.6; H, 0.5; S, 4.5. $C_{19}H_5F_{10}O_2(S_{1.2}Se_{0.8})MoTl$ requires C, 26.6; H, 0.6; S, 4.5%]. NMR [$(CD_3)_2CO$]: ^1H, δ 5.71 (br s, C_5H_5); ^{19}F, δ −124.1 (br d, *o*-F, SeC_6F_5), −130.3 (br t, *o*-F, SC_6F_5), −157.9 (m, *p*-F, SeC_6F_5), −160.0 (m, *p*-F, SC_6F_5), −163.1 (m, *m*-F, SeC_6F_5), −163.9 (m, *m*-F, SC_6F_5). IR: ν(CO) 1953 and 1872 cm^{-1}.

Reaction of [$WBr_3(CO)_2(cp)$] *with* 3 *Equivalents of* $Tl(SeC_6F_5)$.—The compounds [$WBr_3(CO)_2(cp)$] (0.59 g, 1.08 mmol) and $Tl(SeC_6F_5)$ (1.46 g, 3.23 mmol) were stirred in dichloromethane (50 cm^3) for 2 d. The dark brown solution was filtered, centrifuged and concentrated *in vacuo*. Light petroleum was added and the solution cooled to −15 °C affording black needles of [$W(SeC_6F_5)_3(CO)(cp)$] **12**. These were recrystallised from dichloromethane–light petroleum (0.50 g, 46%) (Found: C, 28.1; H, 0.4. $C_{24}H_5F_{15}OSeW$ requires C, 28.4; H, 0.5%). IR (CH_2Cl_2): ν(CO) 2013 cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 5.45 (s, C_5H_5); ^{19}F (18 °C), δ −125.3 (m, 2 *o*-F, *trans*-C_6F_5), −127.8 (br d, 22, 4 *o*-F, *cis*-C_6F_5), −153.4 (t, 20.5, 2 *p*-F, *cis*-C_6F_5) −154.2 (t, 20.6, 1 *p*-F, *trans*-C_6F_5); −161.05 (m, 4 *m*-F, *cis*-C_6F_5), −161.9 (m, 2 *m*-F, *trans*-C_6F_5); ^{19}F (CD_2Cl_2–Et_2O, −100 °C), δ −125.0 (br d, *o*-F, isomer **A**); −125.7 (br d, 24, *o*-F, *trans*-C_6F_5, isomer **B**), −126.4 (br d, *o*-F, isomer **A**), 127.5 (br d, 26, *o*-F, *cis*-C_6F_5, isomer **B**), −128.5 (br d, 28 Hz, *o*-F, *cis*-C_6F_5, isomer **B**), −153 (m, *p*-F, isomers **A** and **B**), −160.0, −160.7 and −161.2 (m, *m*-F, isomers **A** and **B**). After crystallisation of the above product, the remaining solution was concentrated *in vacuo* and cooled to −15 °C. This gave a mixture of dark brown, red and orange crystals. The red crystals were extracted with light petroleum and then recrystallised from dichloromethane–light petroleum affording red needles of [$W(SeC_6F_5)(CO)_3(cp)$] **8b** (8 mg, 1.3%). IR (CH_2Cl_2): ν(CO): 2029, 1942 cm^{-1}. NMR ($CDCl_3$): ^1H, δ 5.75 (s, C_5H_5); ^{19}F, δ −125.3 (m, 2 *o*-F), −154.9 (t, 20.8 Hz, 1 *p*-F), −161.9 (m, 4 *m*-F). MS, *m*/*z* (%, ^{184}W, ^{80}Se): 580 (49, M^+), 552 [27, $(M - CO)^+$], 524 [87, $(M - 2CO)^+$], 496 [100, $(M - 3CO)^+$] and smaller fragment ions.

Preparation of [$TlW(SeC_6F_5)_4(cp)$] **11b**.—The compounds [$W(SeC_6F_5)_3(CO)(cp)$] (0.2 g, 0.20 mmol) and $Tl(SeC_6F_5)$ (0.089 g, 0.20 mmol) were stirred in tetrahydrofuran (40 cm^3) for 4 d. Then $Tl(SeC_6F_5)$ (0.04 g, 0.08 mmol) was added and the solution was stirred for further 2 d. The solution was pumped to dryness and the residue extracted into dichloromethane (100 cm^3), filtered, centrifuged and concentrated *in vacuo*. Addition of light petroleum and cooling to −15 °C caused precipitation of a microcrystalline, red solid (24.3 mg, 8.5%) (Found: C, 23.1; H, 0.2. $C_{29}H_5F_{20}Se_4TlW$ requires C, 24.2; H, 0.35%). NMR: ^1H (CD_2Cl_2), δ 5.51 (s, C_5H_5); ^{19}F ($C_6D_5CD_3$, 40 °C), δ −125.2 [d, *J*(Tl–F) 1312, 8 *o*-F], −153.4 (t, 20.7, 4 *p*-F), −161.3 (m, 8 *m*-F); ^{19}F (CD_2Cl_2, 19 °C), δ −125.3 [br d, *J*(Tl–F) ≈ 1300, 8 *o*-F], −153.6 (t, 20.6, 4 *p*-F), −161.3 (m, 8 *m*-F); ^{19}F (CD_2Cl_2, −60 °C): δ, −124.3 [br dd, *J*(Tl–F) 2528, *J*(F–F) ≈ 29, 4 *o*-F], −126.2 (br t, *ca.* 32, 4 *o*-F), −152.8 (t, 21.4 Hz, 4 *p*-F), −159.8 (m, 4 *m*-F), −161.5 (m, 4 *m*-F).

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