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## Short Communication

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### Pi-bonding effects in organoxytungsten(VI) fluorides

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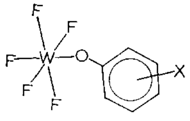
It has been recently suggested that bound oxygen or $\mu$-oxo bonded ligands can alter the electronic environment of a metal in a high oxidation state in such a way as to affect strongly the $^{19}F$ NMR spectrum of fluorine atoms bonded to the metal[1–3]. Studies of the F chemical shift as a function of R and $n$ in the series $(RO)_nWF_{6-n}$ show that the ability of ligands to donate electrons to tungsten(VI) follows the order, $CH_3O > C_6H_5O > F$[2b], however, the increment in chemical shift as $n$ is varied is not linear[4]. We wish to explore the question as to the importance of $\sigma$- and $\pi$-bonding interactions in $\mu$-oxo bonded ligands on transition metals in high valence states. With this aim we are currently investigating by $^{19}F$ NMR spectroscopy the influence of functional groups X bound to selected ring positions for the system,



We report here preliminary results for the case where X = F. Moreover, a directly comparable method has become available, permitting use of pentafluorophenyl derivatives as probes for quantifying inductive and tautomeric effects of various metallic substituents[5,6]. We therefore include initial NMR parameters obtained for the compound $C_6F_5OWF_5$ with the present discussion.

Straightforward analysis of the $-OWF_5$ group viewed as a substituent on fluorobenzene results in inductive[7a] and resonant[7b] substituent constants calculated from our data in Table 1 and the equations given by Taft *et al.*[7]; thus $\sigma_I = +0.91$, $\sigma_R{}^\circ = +0.065$. The high positive value of $\sigma_I$ confirms the very pronounced $\sigma$ electron-withdrawing character expected for tungsten(VI), and can be compared to values reported[7] for $-OCF_3$, $-SF_5$, $-CN$, or $-NO_2$ groups which afford inductive constants ranging from about +0.5 to +0.65. For closer comparison, the positively charged $-N(CH_3)_3{}^+$ substituent has $\sigma_I = +0.93$. That the

$\mu$-oxo linkage itself is not primarily responsible for the large positive $\sigma_I$ value can be seen by comparison[7] of the groups $-CH_3$ and $-OCH_3$; $-CF_3$ and $-OCF_3$; $-C_6H_5$ and $-OC_6H_5$; $-H$ and $-OH$. In each case the value of $\sigma_I$ is seen to increase by approximately 0.25 in going from $-R$ to $-OR$.

TABLE 1

FLUORINE MAGNETIC RESONANCE PARAMETERS FOR $X-C_6H_4OWF_5$ COMPOUNDS

| | X = H | *ortho*-F[f] | *meta*-F[g] | *para*-F[h] | |
|---|---|---|---|---|---|
| $\delta(F_{axial})$[a] | 53.51 | 45.73 | 44.06 | 49.41 | ppm |
| $\delta(F_{equatorial})$[a] | 39.01 | 33.59 | 35.48 | 37.93 | ppm |
| $J(F_{ax.}-F_{eq.})$[b] | 64.67 | 64.73 | 64.56 | 64.58 | Hz |
| $\delta(F_{aromatic})$[c] | — | −37.45 | −55.88 | −57.79 | ppm |
| r.m.s. error[d] | 0.19 (12) | 0.45 (11) | 0.30 (18) | 0.105 (28) | Hz |
| $\delta(F_{aromatic})$[e] | — | 12.54 | −5.89 | −7.80 | ppm |

[a] $\delta(WF_6)_{internal} = 0$ ppm, upfield = +; note that $\delta(WF_6)_{int.} = \delta(C_6F_6)_{int.} - 329.5 \pm 0.3$ ppm.

[b] $J$ = Hertz, estimated uncertainty $\pm < 0.2$ Hz.

[c] $\delta(C_6F_6)_{int.} = 0$ ppm, upfield = +.

[d] r.m.s. error of overall computer fit, number of lines fitted in brackets.

[e] Where $\delta(C_6H_5F)_{external} = 0$, as calculated from $\delta(C_6H_5F)_{int.} = \delta(C_6F_6)_{int.} - 49.99$ ppm.

[f] *Ortho*-F shows unresolved coupling into ring from $WF_5$ group, principally *axial*-F.

[g] Also 0.8 Hz coupling to *meta*-F from *axial*-W–F; $J(F_m-F_{eq.})$ not > 0.25 Hz.

[h] Also 2.33 Hz coupling to *para*-F from *axial*-W–F.

The effective[7b] resonance parameter of +0.065 demonstrates more dramatically the dominance of the $-WF_5$ moiety in the $-OWF_5$ substituent effect. A positive value again indicates electron-withdrawal, but now predominantly *via* $\pi$-type interactions. Again the $-OWF_5$ group is seen to be similar to the $-CN$ or $-NO_2$ groups, whose resonant parameters are about +0.2, but it more closely resembles the perfluoro ligands $-CF_3$ (+0.11) or $-SF_5$ (+0.088). In contrast, the common oxo-bridged species, hydroxy, alkoxy, and aryloxy, are all $\pi$-donors, with $\sigma_R{}^\circ$ values around −0.2 to −0.4. This inversion of character of the oxo bridge from $\pi$-donor to $\pi$-acceptor requires either a strong $\pi$ or polar interaction between the $WF_5$ function and oxygen. Evidence of a strong $\pi$ interaction is seen in the intense charge-transfer spectra characteristic of $ArO-W^{VI}$ species[8]. One can readily postulate interaction of the empty d$\pi$ orbitals ($t_{2g}$) on tungsten with suitable filled p- or $\pi$-type orbitals on oxygen; however, in the absence of precise information concerning the geometry about oxygen and the metal, quantitative estimates of the various possible orbital overlaps do not yet seem profitable. We note in this connection the significance of the recent suggestion that d$\pi$–p$\pi$ delocalization attends the observed co-planarity of $C_2N-W-NC_2$ framework and rather short W–N bond distances found in the octahedral $(Me_2N)_6W$ molecule[9].

A generally similar picture for the substituent effects of $-OWF_5$ on the perfluoro aromatic nucleus is obtained from the application of the relationships between $\sigma_I$ and $\sigma_R{}^\circ$ and aromatic $^{19}F$ chemical shifts and $J(2,4)$ developed by Hogben and Graham[5a]. For $C_6F_5OWF_5$ we observe $\delta_p = 150.70$, $\delta_m = 160.22$, $\delta_o = 151.34$, $J(3,4) \sim +19.6$, and $J(2,4) \sim +1.25$*, whence we calculate $\sigma_I \overset{\sim}{<} +0.5$ and $\sigma_R{}^\circ \overset{\sim}{>} -0.1$. We believe these results are not disparate from the foregoing Taft values in that indication of the general character of $OWF_5$ as a strongly $\sigma$-withdrawing moiety is sustained. The apparent inversion in $\sigma_R{}^\circ$ from a $\pi$-acceptor to a $\pi$-donor partly involves experimental errors, but the difference is probably real and represents significant polarity differences induced in the (aromatic) C—O—W framework by the relatively high electronegativity of $C_6F_5$ as compared with $F\text{-}C_6H_4$[5b].

It should be noted here that positive values for $\sigma_R{}^\circ$ indicate *meta*-directing substituents in electrophilic substitution, but to date, no such substitution reactions have been attempted with $ArOWF_5$ compounds. Mortimer and Strong, however, have carried out both nitration and bromination of hexaphenoxytungsten(VI), and found *ortho–para* substitution, but no *meta* isomers. It would be of some interest, therefore, to measure the $^{19}F$ chemical shift parameters for the (presently unknown) *meta* and *para* isomers of $(F\text{-}C_6H_4O)W(OPh)_5$, for which preparative routes are currently under study in these laboratories.

Also of substantial interest is the effect of the various organoxy groups viewed as substituents on $-WF_5$. Chemical shift values for the various $RO\text{-}WF_5$ species thus far reported, as well as those newly prepared in this work, are collected in Table 2. The overall trend in $^{19}F$ chemical shifts is seen to follow, qualitatively, the expected R group electronic properties. In particular, the strongly electron-donating $-OCH_3$ group causes the greatest upfield shift, and replacement of a proton by $CF_3$ in the $CF_3CH_2O-$ case results in a marked downfield shift for *both* W–F (equatorial) and W–F (axial). The effect of chlorine, generally regarded as electron-withdrawing, does not appear to fit into the pattern established by RO–substituents and its mode of interaction with $-WF_5$ requires further study. Within the phenoxy series a similar, but less pronounced trend is also evident, with increasing fluorine substitution causing diminishing upfield chemical shifts. The situation with $C_6F_5O-$ is limiting in the sense that the apparent electron-withdrawal imparted by this substituent affects about equally both axial and equatorial fluorine atoms on the metal.

A somewhat more detailed examination of the bonding within the $WF_5$ group also appears possible on the basis of similar simple concepts. In this connection we examine the W–$\underline{F}$ resonance parameters for the *meta* and *para* isomers of $F\text{-}C_6H_4OWF_5$, adopting the point of view of phenoxy substituents on $WF_5$, rather than the converse situation discussed before. Further, we assume that the differences in W–$\underline{F}$ shift parameters from the *meta-* to the *para*-fluorophenoxy

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* Chemical shifts are relative to internal $C_6F_6$ at $\delta = 163.0$ ppm[5a]; values for $J$ (Hz) are only approximate pending solution of the complex AA′GG′MVX$_4$ spectrum for this compound.

TABLE 2

FLUORINE MAGNETIC RESONANCE SHIFT PARAMETERS FOR $LWF_5$[a]

| L | F(*equatorial*) | F(*axial*) | Reference |
|---|---|---|---|
| $CH_3O$ | 48.7 | 80.8 | 13 |
| $CF_3CH_2O$ | 32.3 | 46.1 | 12 |
| Cl | -16 (4) | 39 | 14 |
| $C_6H_5O$ | 39.01 | 53.51 | [b], 2(b), 12 |
| *o*-$FC_6H_4O$ | 33.59 | 45.73 | [b] |
| *m*-$FC_6H_4O$ | 35.48 | 44.06 | [b] |
| *p*-$FC_6H_4O$ | 37.93 | 49.41 | [b] |
| $C_6F_5O$ | 20.56 | 24.11 | [b,c] |

[a] Shifts are in ppm upfield from $WF_6$. Estimated errors are ± 1 in the last place or less except where indicated.

[b] Present work.

[c] Based on computer fit for $VX_4$ case with three iterations, r.m.s. error = 1.7 Hz.

derivatives are due solely to resonance or $\pi$ interactions, just as is commonly taken for the aromatic F shifts[7]. In the present case, moreover, we have spatially distinct probes in the axial W–$\underline{F}$ and equatorial W–$\underline{F}$ resonance positions, consequently, comparatively independent estimates of the $\pi$ interaction with ligands disposed on tungsten either as F–W–F or ($FC_6H_5O$)–W–F in *cis* or *trans* geometries are possible. Parshall has demonstrated the utility of a similar approach in rationalizing the *trans* effect for square-planar $Pt^{II}$ compounds[6a].

For $-WF_5$ these differences from *meta* to *para* isomers are +5.35 ppm for the W–F (axial) and +2.45 ppm for W–F (equatorial), with the *para* isomer resonance at higher field in both cases. It should be mentioned that this upfield shift for the *para* isomer is to be expected, since fluorine is a $\pi$ donor, although the net $\sigma + \pi$ effect is one of strong electron withdrawal. It thus appears that the $\pi$ effect on axial fluorine is roughly twice that observed for the equatorial fluorine, a result which can be rationalized in terms of the number of d$\pi$ orbitals of appropriate symmetry on tungsten available for effective overlap with *cis* and *trans* ligands. This effect has been invoked[10] to explain isomer distributions in certain $d^0$ oxo–metal halide complexes, but a more quantitative basis has been established from a correlation of $^{19}F$ chemical shifts and substituent constant values for the series $TiF_4$–2L[3b].

The new compounds listed in Table 1 were prepared[2b,4] by treatment of the appropriate fluorophenoxytrimethylsilane[11] with excess $WF_6$ in perfluorobenzene solvent. Reactions were complete in several days and, following removal *in vacuo* of volatile product $Me_3SiF$, solvent and unreacted $WF_6$, each deep-red product was sublimed to yield (>90%) the fluorophenoxytungsten(VI) pentafluoride for which a satisfactory elementary analysis was obtained. All sealed NMR tubes were made up at comparable concentrations (~ 50 wt.%) of phenoxy isomer in $C_6F_6$ with smaller amounts of $WF_6$ and $Me_4Si$ added ($ArOWF_5:WF_6:TMS = 0.70:0.20:0.10$) as internal references. A similar tube containing only $C_6H_5F$, $C_6F_6$ and $WF_6$ (0.50:0.40:0.10) allowed the measurement of the chemical shift of $C_6H_5F$ (protons decoupled) from $C_6F_6$ as −49.99 ppm. This value was then subtracted from the measured internal shift of the aryloxytungsten compound relative to $C_6F_6$ to give the shift of the aryl fluorine from fluorobenzene (Table 1). NMR spectra obtained at 56.44 Hz for $Ar\text{-}\underline{F}$ and $W\text{-}\underline{F}$ were complex, requiring computer solution of non-first order effects. The results so obtained are summarized in Table 1 along with estimated r.m.s. errors derived from fits. Pentafluorophenoxytungsten(VI) pentafluoride was not isolated, but studied as a freshly prepared solution obtained from the corresponding siloxane[5a] treated with a two-fold excess of $WF_6$ in $C_6F_6$. The reaction was quantitative in two days, yielding a clear red-orange solution of approximately the same concentration [along with $(CH_3)_3SiF$] indicated above. Its NMR spectrum was obtained at 84.67 MHz.

In conclusion, $\pi$-bonding effects in organoxytungsten(VI) fluorides seem to be important and more work, some of which is in progress with related compounds, is needed for definitive answers.

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