Evidence for multiple bonding in metal-to-fluoroalkyl bonds

Several recent notes[1–3] have offered evidence that certain metal–perfluoroalkyl ($M-R_F$) bonds are stronger than the corresponding metal–alkyl (M–R) bonds are known or expected to be, and have attributed this to partial metal-to-carbon multiple bonding. In several cases reference has been made to what appears to be the first suggestion[4] of such multiple bonding.

This original suggestion was offered without explicit documentation in the expectation of prompt completion and full reporting of the work on which it was based. As the completion of that work has been delayed, while the idea itself has become a subject of some interest, this note provides a brief account of the evidence underlying the suggestion. A full account[5] will be submitted as soon as possible.

The strongest evidence comes from the infrared spectrum of $CF_3Mn(CO)_5$ in the regions of the internal modes of the CF_3 group. From 400 to 1300 cm^{-1} the following bands (in cm^{-1}) are observed (CS_2 solution): 1053 (s), 1018 (s), 782 (s), 762 (m), 694 (w), 652 (sh), 646 (s). Since $BrMn(CO)_5$ has a strong band at 638 cm^{-1}, we assume that one or both of the last mentioned bands of $CF_3Mn(CO)_5$ are due to the $Mn(CO)_5$ group, probably to an Mn–C–O wagging mode. The remaining five bands seem to be attributable to the CF_3 group. When these are compared to the modes of a CF_3 group in various CF_3X compounds such as those[6] in which X is Cl, Br, or I, it is evident that extensive shifts have occurred. Here we shall discuss only the C–F stretching modes, which are found at 1177–1217 (E) and 1058–1104 (A_1) wave numbers in the CF_3 halides. It thus appears that in $CF_3Mn(CO)_5$ these modes have been lowered by, on the average, about 100 cm^{-1}. Since the mean frequency in the CF_3X compounds is $\sim$ 1140 cm^{-1}, this indicates, roughly, a drop of about 10 % in the C–F force constant. We suggest that this is due to a drift of electrons from the appropriate d_π orbitals of Mn (d_{xz}, d_{yz}) into the C–F antibonding orbitals (a set with quasi-E symmetry) of CF_3.

It is interesting to note that if the $M-R_F$ bond shortenings[1–2], 0.10 Å, are used to estimate the M–C bond order increases over 1.0, according to a recently published correlation[7] an increase of $\sim$ 15 % can be estimated. This is not inconsistent with the preceding deduction from the decrease in C–F force constants.

Similar shifts of C–F frequencies have been observed in other $R_F-M(CO)_n$ compounds, such as $CF_3Fe(CO)_4I$. Moreover, there are large shifts also in F–C–F deformation frequencies, but the detailed interpretation of all these shifts requires complete data and an approximate normal coordinate analysis[5].

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